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DEVELOPMENT OF A MOLTEN CARBONATE PROCESS FOR REMOVAL OF SULFUR DIOXIDE FROM POWER PLANT STACK GASES

PROGRESS REPORT NUMBER 2
PART I. PROCESS CHEMISTRY – REDUCTION
April 1, 1968 to October 27, 1968

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SUMMARY

In the Molten Carbonate Process, the flue gases are scrubbed with a melt of alkali metal carbonates. This produces a melt mixture of alkali metal carbonates, sulfites, and sulfates, which must be treated to regenerate the carbonate and recover the sulfur. The first step of the treatment is the chemical reduction of the sulfite and sulfate to sulfide, using hydrogen, carbon monoxide, or carbon as the reducing agent. The chemistry of the hydrogen reduction step was studied in detail. It was found that the reduction was zero-order with respect to sulfate concentration, and that the rate was catalyzed by iron, and autocatalyzed by the sulfide product. An expression for the rate of reduction with hydrogen was derived; it is

$$\text{rate} = K(T)[M_2SO_4]^{0.0}\,[M_2S]^{0.37}\,[0.7 + (Fe)^{0.41}]\,[H_2]^{0.65}$$

Increasing the temperature 100°C quadruples the reaction rate if no iron catalyst is present, and doubles the iron-catalyzed rate. The following conclusions were drawn concerning the reduction reaction mechanism: (1) the reaction does not take place in the gas phase, (2) sulfate and sulfide combine to form the intermediate that undergoes reduction in the rate determining step, and (3) the role of iron is one of either stabilizing the reactive intermediate (thus increasing its concentration) and/or acting directly in the reduction of the intermediate.

Studies with carbon monoxide indicate it is not as reactive as hydrogen. However, its reactivity increases with pressure more rapidly than hydrogen, so it may be useful at high pressures. At temperatures above 700°C (~1300°F), carbon is an excellent reducing agent. At 800°C (1472°F) complete reduction was obtained in 14 minutes using fluidized petroleum coke and an iron catalyst.

Present recommendations are to use hydrogen at 600°C (1110°F), 10 atm, 9% sulfide catalyst, and 2% iron catalyst, for a reaction time of 40 minutes, or else fluidized coke at 800°C (1382°F), 1 atm, and 2% iron catalyst for a 15 minute reaction time.

I. INTRODUCTION

The Atomics International Molten Carbonate Process takes advantage of rapid reaction between sulfur dioxide and a eutectic mixture of molten lithium, sodium, and potassium carbonates to remove the sulfur dioxide from flue gas. The reaction yields the alkali metal sulfites:

$$M_2CO_3 + SO_2 \xrightarrow{450°C} M_2SO_3 + CO_2 \qquad (1)$$

where M represents the eutectic mixture of lithium, sodium, and potassium cations. The metal sulfite subsequently disproportionates to the sulfate and sulfide upon heating:

$$4\ M_2SO_3 \xrightarrow{600°C} 3\ M_2SO_4 + M_2S. \qquad (2)$$

To allow reuse of the valuable salts, the sulfate is next reduced to sulfide:

$$M_2SO_4 + \begin{matrix} 4H_2 \\ 4\ CO \\ 2\ C \end{matrix} \xrightarrow{600\text{-}800°C} M_2S + \begin{matrix} 4H_2O \\ 4\ CO_2 \\ 2\ CO_2 \end{matrix} \qquad (3)$$

Finally the sulfide is regenerated to the metal carbonate and hydrogen sulfide by the reaction

$$M_2S + CO_2 + H_2O \xrightarrow{450°C} M_2CO_3 + H_2S. \qquad (4)$$

The carbonate is returned to the absorber for reuse. The hydrogen sulfide is further processed to salable elemental sulfur or sulfuric acid.

The reduction step (Equation 3) is the subject of this report. Some of the reduction work was done during the previous report period; these early results are included wherever it is necessary for completeness.

A. BACKGROUND

The reduction of sodium sulfate to sodium sulfide has been accomplished with carbon monoxide(2, 10, 17, 19, 39, 40, 46); hydrogen(14, 16, 17,

24, 27, 36, 37, 46, 47, 48); natural gas and methane(2, 13, 17, 24, 27, 33, 36); producer gas and water gas(18, 19, 27, 36); and carbon(9, 17, 25, 29, 30, 34, 42) in the form of graphite(6, 7), gas black(6, 7), coal(5, 11, 15, 46), charcoal(7, 8, 40), and coke(2, 8). In addition, hydrogen sulfide and ammonia(32) have been mentioned as reducing agents. Since very few of the publications compare one reductant with another and since there is considerable contradiction between workers, it is quite difficult to compare the various reducing agents based upon a review of the literature. In addition, comparisons between solid (i.e., carbon) and gaseous (e.g., hydrogen) reducing agents are difficult to establish. But based upon temperatures at which the reductions were carried out, it appears that the reactivity decreases in the following order:

1. Hydrogen
2. Carbon (excluding graphite)
3. Carbon Monoxide
4. Hydrogen Sulfide
5. Ammonia
6. Natural Gas and Methane
7. Graphite

Graphite only begins to react with sulfate at 880°C(6, 7) and for this reason it is recommended as a container for sulfate reduction reactions below 800°C(1,46).

Although considerable discrepancy exists in the literature concerning reduction temperatures and rates, temperatures between 750°C and 900°C are frequently cited as the most ideal. Temperatures in the 600°C range have

been utilized at the expense of longer reaction times(18, 47, 48), while temperatures above 900°C have caused numerous side reactions(6, 7, 10, 13, 46)*. In the reduction of sodium sulfate (m.p. = 884°C) to sodium sulfide (m.p. 1180°C) the reactant-product mixture passes through a eutectic composition (43% Na_2S - 57% Na_2SO_4, m.p. = 665°C - Ref. 37). Thus, the physical nature of the system may change from a solid to a liquid and back to a solid during the course of the reduction. The exact effect this has on the reaction rate is difficult to evaluate due to the complex reaction mechanism. It appears, however, that the largest effect is on the rate of mass transfer between the phases. In other words, the phase of the sulfate-containing medium which proves to be the most reactive is that phase which gives the best contact between the reducing agent and the sulfate. Thus, the liquid phase is better when carbon is used(11, 46) and the solid phase is better for hydrogen reductions(46).

Catalysts for the reduction of sulfate fall into four general categories. These are: (1) transition-metal compounds(2, 7, 10, 16, 19, 36, 37); (2) sulfide autocatalysis(40); (3) species that change the phase of the sulfate-containing medium, e.g., carbonate(11, 47, 48) and sulfide(6); and (4) carbon, used mainly in the form of activated charcoal(7, 10). As far as the transition-metal compounds are concerned, iron has been demonstrated

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*It is interesting to note at this point that sodium sulfate can be reduced at ambient conditions by some bacteria, e.g., Desulfovibrio desulfuricans (44, 45). In fact, it is these species that give certain swampy areas their characteristic odor.

to be the most useful(2, 14, 36, 37) for all of the reducing agents. Although no explanation has been given for the catalytic activity of iron, it appears that the iron-containing species (as opposed to the reducing agent) must interact with the sulfur-containing species, since the catalytic activity is universal with all reported reducing agents.

Only brief and incomplete information has been presented concerning flow rate, gas pressure, surface area, reactor design, impurities, etc. As a result, any mechanistic information presented could only be speculative. Thus, the most discussed mechanism was the one that appeared most logical; that is, the bimolecular reduction of sulfate with hydrogen to form sulfite and the subsequent disproportionation of sulfite to sulfide and sulfate(15, 35, 42). This mechanism, assuming the rate-determing-step is the sulfate-hydrogen interaction, would result in a kinetic expression that would be first order with respect to both sulfate and hydrogen.

Preliminary work at Atomics International(3, 22, 24) was directed toward obtaining a rapid reduction at relatively low temperatures. This effort was carried out because the carbonate-sulfate-sulfide melts are quite corrosive to construction materials (with the corrosion rate rapidly increasing with temperature) and because slow reactions would create large inventories of melt and would result in increased capital and operating costs of the process. The investigations by Grantham et al were concerned with various reducing agents(21, 23), temperature effect(21), catalytic activity(22) and pressure effect(21). Birk, in his preliminary work(3), compared the reducing

activity of hydrogen and charcoal; investigated the effect of surface area and contact; and developed the analytical techniques for monitoring the reduction.

The preliminary AI work demonstrated that the reaction time was quite long using either charcoal(3), carbon monoxide(3, 21), or hydrogen(3, 21) at temperatures less than 600°C. In fact, reaction times on the order of one to two days were common with bubble-type contacting. Catalysts containing molybdenum, cobalt, tungsten and nickel were not found to improve the rate significantly(22); however, increased pressure in carbon monoxide reductions(21) and increased surface area with hydrogen reduction(3) enhanced the rate considerably. Using metal packing in a rotating bomb, the reaction time with hydrogen was on the order of one hour at 600°C(3).

B. PURPOSE OF THIS INVESTIGATION

The ultimate application of knowledge gained through study of sulfate reduction will be the design of the reducer reactor for a commercial Molten Carbonate Process plant. The design of this reactor requires an understanding of the overall reaction kinetics of the reduction, which will determine gas and liquid flow rates as well as reactant residence time in the reactor.

The effects of variables including reactant concentrations, temperature, catalyst species (physical and chemical form and concentration), degree of agitation, and operating pressure can influence the rate of reduction.

The purpose of this investigation was thus to determine the effects of the inter-related variables which control the rate of reduction reaction and specify the detailed form of the overall reaction rate expression.

C. THERMODYNAMICS

The enthalpy and free energy of the reduction reaction were calculated from the heats and free energies of formation of the reactants and products given in Table I. The free energy (ΔF_f) and enthalpy (ΔH_f) of the reduction reaction with hydrogen are presented as a function of temperature in Fig. 1 and Table II. Table II also contains the free energy and enthalpy changes for the reduction reaction with carbon monoxide and carbon. The thermodynamic values of the above reactions are compared with those of other reducing agents at 627°C in Table III.

These calculated thermodynamic values show that hydrogen, carbon monoxide, carbon, methane, and ammonia are potential reducing agents. However, the last three enter into reactions that are quite endothermic. The reduction with hydrogen sulfide to form elemental sulfur is unfavorable from both free energy and enthalpy considerations.

TABLE I.

Heats and Free Energies of Formation (43)*

Cmpd.	Item	25°C	327°C	427°C	527°C	627°C	727°C	827°C
$Na_2SO_4(\ell)$	ΔH_f	324.24	325.02	324.53	336.94	335.67	334.43	333.22
	ΔF_f	298.17	271.17	262.20	254.61	244.40	234.32	224.37
$Na_2S(\ell)$	ΔH_f	87.87	90.46	90.57	103.65	103.33	102.99	102.66
	ΔF_f	85.46	81.67	80.18	79.96	77.01	74.11	71.24
$H_2O(g)$	ΔH_f	57.80	58.50	58.71	58.91	59.08	59.25	59.39
	ΔF_f	54.64	51.16	49.92	48.65	47.35	46.04	44.71
$CO_2(g)$	ΔH_f	94.05	94.12	94.17	94.22	94.27	94.32	94.37
	ΔF_f	94.27	94.46	94.51	94.56	94.60	94.63	94.66
$CO(g)$	ΔH_f	26.42	26.33	26.41	26.51	26.64	26.77	26.91
	ΔF_f	32.78	39.31	41.47	43.61	45.74	47.86	49.96
$CH_4(g)$	ΔH_f					21.21		
	ΔF_f					-2.03		
$NH_3(g)$	ΔH_f					13.29		
	ΔF_f					-12.10		
$H_2S(g)$	ΔH_f					21.40		
	ΔF_f					10.94		

*Heats and free energies of all the elements ($H_2(g)$, $S_2(g)$(627°C), C(s), and $N_2(g)$ are zero. All numbers in the table are negative values.

TABLE II.

Heats and Free Energies of Reaction

Reaction	Item	25°C	327°C	427°C	527°C	627°C	727°C	827°C
$Na_2SO_4(\ell) + 4H_2(g) \rightarrow$	ΔH	+5.17	+0.56	-0.88	-2.35	-3.98	-5.56	-7.00
$4H_2O(g) + Na_2S(\ell)$	ΔF	-5.85	-15.14	-17.66	-19.95	-22.01	-23.95	-25.71
$Na_2SO_4(\ell) + 4CO(g) \rightarrow$	ΔH	-34.15	-36.60	-37.06	-37.55	-38.18	-38.76	-39.28
$4CO_2(g) + Na_2S(\ell)$	ΔF	-33.25	-31.10	-30.14	-29.15	-28.05	-26.87	-25.67
$Na_2SO_4(\ell) + 2C(s) \rightarrow$	ΔH	+48.27	+46.32	+45.62	+44.85	+43.80	+42.80	+41.82
$2CO_2(g) + Na_2S(\ell)$	ΔF	+24.17	+0.58	-7.00	-14.47	-21.81	-29.05	-36.19

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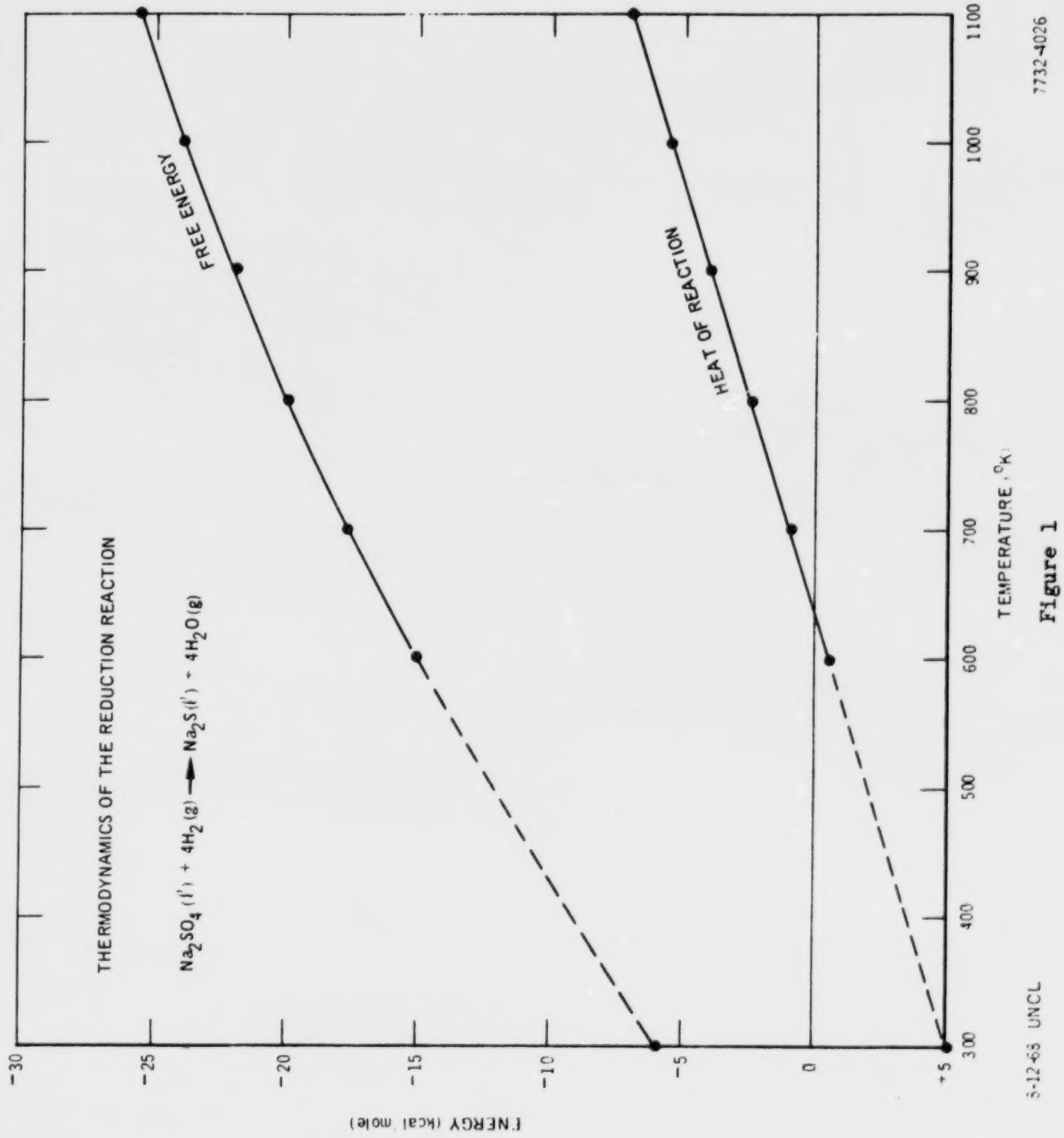
THERMODYNAMICS OF THE REDUCTION REACTION
Na_2SO_4 (l) + $4H_2$ (g) → Na_2S (l) + $4H_2O$ (g)
FREE ENERGY
HEAT OF REACTION
ENERGY (kcal/mole)
TEMPERATURE, °K
-30
-25
-20
-15
-10
-5
0
+5
300
400
500
600
700
800
900
1000
1100
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Figure 1

TABLE III.

Thermodynamic Values of the Reduction of Sulfate with Various Reducing Agents (627°C)

Reaction	ΔH Kcal	ΔF Kcal
$Na_2SO_4(\ell) + 4H_2(g) \longrightarrow 4H_2O(g) + Na_2S(\ell)$	-3.98	-22.01
$Na_2SO_4(\ell) + CO(g) \longrightarrow 4CO_2(g) + Na_2S(\ell)$	-38.18	-28.05
$Na_2SO_4(\ell) + 2C(s) \longrightarrow 2CO_2(g) + Na_2S(\ell)$	+43.80	-21.81
$Na_2SO_4(\ell) + 4C(s) \longrightarrow 4CO(g) + Na_2S(\ell)$	+125.78	-15.57
$Na_2SO_4(\ell) + CH_4(g) \longrightarrow 2H_2O(g) + CO_2(g) + Na_2S(\ell)$	+41.12	-23.94
$Na_2SO_4(\ell) + 8/3NH_3(g) \longrightarrow 4H_2O(g) + Na_2S(\ell) + 4/3N_2(g)$	+31.46	-54.28
$Na_2SO_4(\ell) + 4H_2S(g) \longrightarrow Na_2S(\ell) + 4H_2O(g) + 2S_2(g)$	+81.62	+21.75

II. EXPERIMENTAL

A. REAGENTS AND APPARATUS

All chemicals used in this work were reagent grade. The fluidized coke was obtained from Phillips Petroleum Company (Control Laboratory, Martinez, California 94553). The properties of this material are given in Table IV.

TABLE IV.

Properties of Fluidized Coke

Sulfur (wt%)	1.39
Bulk Density (g/cc)	0.85
Screen Analysis (wt%)	
Greater than 4 mesh	1.9
Greater than 80 mesh	30.2
Greater than 100 mesh	55.9
Greater than 200 mesh	99.0
Ash (wt%)	0.39
Volatile Combustibles	4.56
H_2O (wt%)	0.62
"Fixed Carbon"	94.43
Heating Value (Btu/lb.)	14,600

Figure 2 gives a schematic representation of the experimental set-up used for both gaseous and fluidized coke reductions. Figure 3 shows a schematic of the reaction vessel used for the reduction experiments. The important features of the reaction vessel are as follows: (1) the metallic part can be reused; (2) the melt contacts only the graphite; (3) the vessel can be

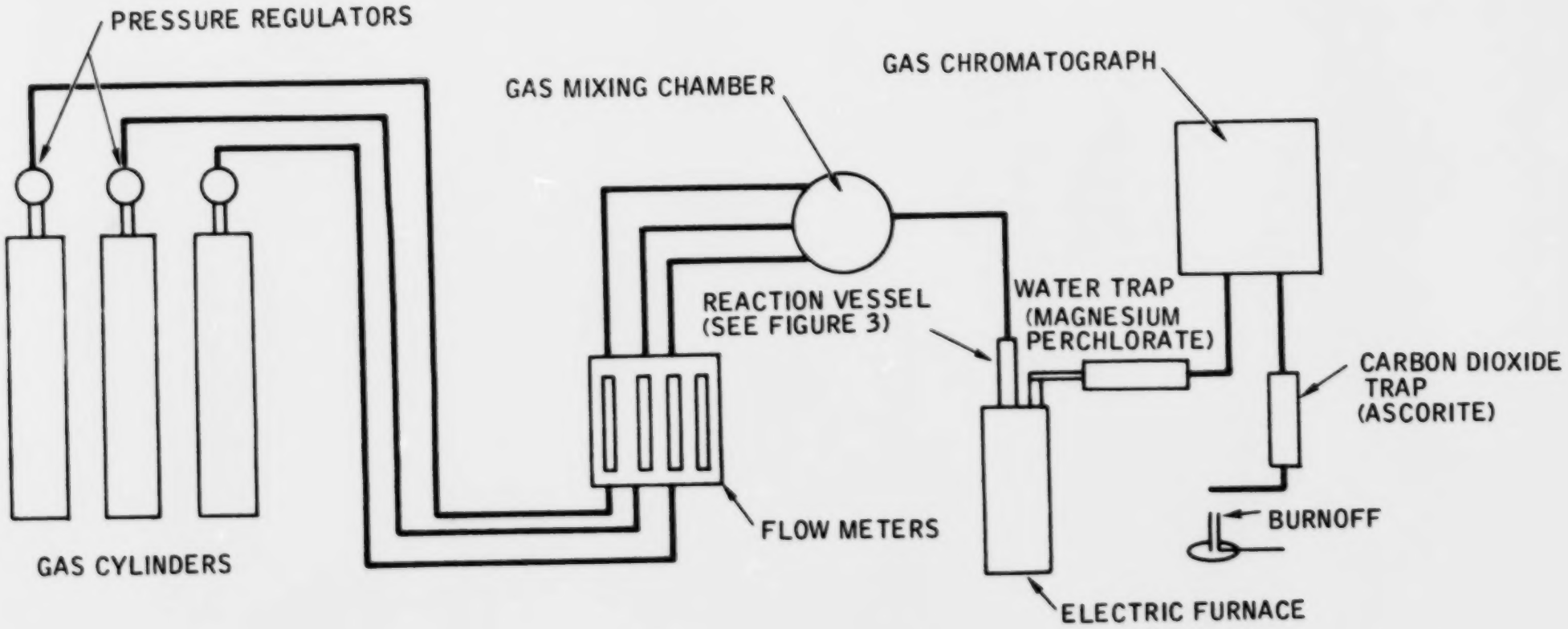

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Figure 2. Schematic Diagram of Apparatus

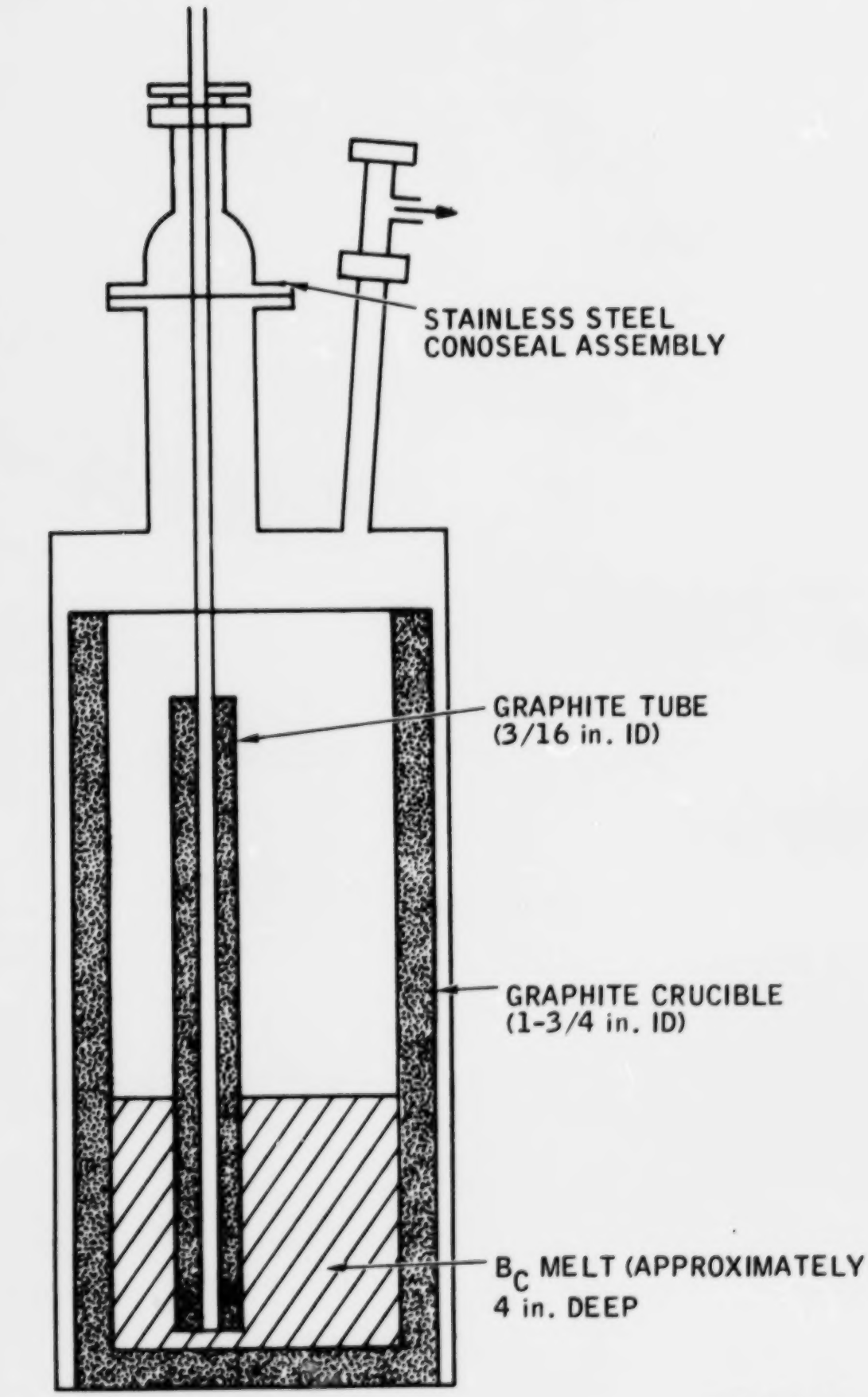

Figure 3. Schematic of Reaction Vessel

opened at the Conoseal Assembly during the course of a test for visual inspection; and (4) melt samples can be taken easily through the gas exit line. The impurities (nominal values) in the graphite are given in Table V.

TABLE V.

Nominal Impurities in the Graphite Crucible

Impurity	Concentration
Si	0.04%
Fe	0.04%
Cu	0.03%
Al	0.03%
V	0.007%
Ash	0.2%
S	0.1%

B. PROCEDURE

The procedure used in all tests is described below. The graphite crucible was washed with 1:1 HCl, distilled water, acetone and dried with a stream of air. The salt (weights for each test are given in Table A-1 in the Appendix) was weighed, mechanically mixed, and placed in the graphite crucible. The crucible was placed in the stainless steel bomb which was subsequently welded shut. The bomb was placed in the furnace and brought to temperature under a continuous stream of argon or helium. After the melt was at temperature, a sample was taken by drawing up a portion (4-7 grams) of melt into a 4 or 5mm quartz tube. The bomb was sealed (except for the inlet and exit gas lines) and the reactant gases were passed through the melt at

a rate of 1.4 ℓ/min (unless otherwise indicated). The heat evolved from the water and/or carbon dioxide traps gave an indication of the rate of reduction during the course of the experiment, and melt samples were taken periodically (depending upon the rate) while at the same time the various gas traps were weighed. During sampling an inert gas was passed through the melt.

Samples were analyzed for sulfate by the usual gravimetric barium sulfate precipitation. Total sulfurs were done by bromine oxidation in basic solution and subsequent barium sulfate precipitation. A recently developed, but not yet published (31), gas chromatographic technique was used for the analysis of sulfite, sulfide, and carbonate. The technique depends upon the evolution of the respective gases (SO_2, H_2S and CO_2), which are separated and analyzed by the gas chromatograph. Accuracy of the techniques is $\pm$ 6% for sulfite and sulfide, and $\pm$ 2% for carbonate, sulfate and total sulfur. Iron analyses were done by the standard colorimetric procedure using 1,10 phenanthroline.

III. RESULTS AND DISCUSSION

Many of the experiments were done with the purpose of determining the effect of a single variable (e.g., temperature, pressure, or catalyst) on the reduction rate. A comparison of the results of these tests is presented in this section in tablulated and graphical form. The graphical presentations are plots of percent reduction vs. time and the tabulations are comparisons of the average reduction rate (usually determined between 25 and 75 percent completion) as a function of the independent variable of interest. The data from each experiment are presented in Table A-2 of the Appendix.

Since sulfate analysis were found to be most reliable, these results were used to calculate the percent reduction. However, in almost every case the percent reduction based on sulfide results, water-evolution data, and/or on carbon dioxide-evolution data compared quite closely with that based upon sulfate results.

The average rate of reduction was arbitrarily defined as the average rate between the time 25% of the sulfate was reduced and the time when 75% of the sulfate was reduced. This method of calculating the average rate eliminated, for a large part, the initial slow rate caused by autocatalysis; it should be typical of the rate encountered in an actual continuous process under like conditions.

A. HYDROGEN REDUCTIONS

1. Transition Metal Catalysis

The use of several transition-metal compounds and some alkali metal compounds as catalysts was investigated at 600° C. Compounds containing iron (Expt.3), copper (Expt. 7), chromium (Expt. 8), manganese (Expt. 9), nickel (Expt. 11), tin (Expt. 13), molybdenum (Expt 15), vanadium (Expt. 16), titanium (Expt. 20), cobalt (Expt. 22), germanium (Expt.23),and rubidium (Expt. 27) were tried in quantities of about five mole percent. The results of these tests are compared with one another and a control (Expt. 2) in Table VI and Fig. 4.

TABLE VI

Transition Metal Catalysis

Catalyst	Average Rate %/hr.)
None	2.9
$FeSO_4$	17.2
Mo	3.4
$VOSO_4$	3.5
$CoSO_4$	3.7
$SnSO_4$	7.4
Rb_2O	3.4

The results of these tests demonstrate that only tin and iron are significantly effective for catalyzing the reduction. Although molybdenum appears useful from the figure, it was added as the metal and as a result undoubtedly took some part in reducing the sulfate. This may also explain the atypical reduction curve noted in the molybdenum test.

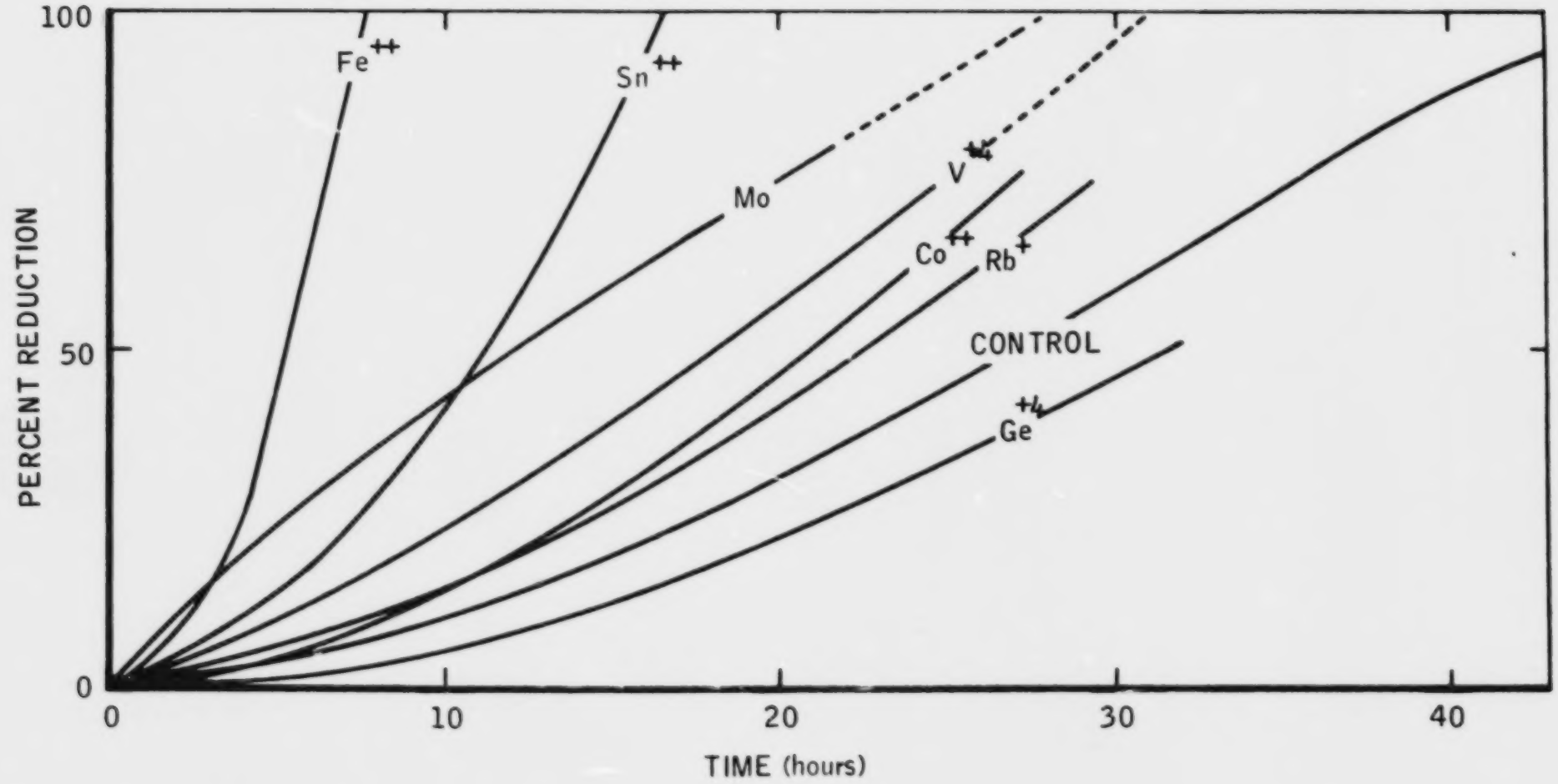

Figure 4. Comparison of Catalysts for the Reduction of Sulfate with Hydrogen at 600°C

2. Effect of Temperature

The effect of temperature on the rate of the uncatalyzed reduction was investigated in Tests 2, 6, 42, 54 and 61. A summary of the results from these experiments is given in Table VII and Figure 5.

Table VII

Effect of Temperature on Reduction Rate

Temperature (°C)	Rate (%/hr)
600	2.9
650	8.2
700	14.7
750	24.0
840	(88)

( ) Estimate based upon incomplete reduction data.

These results show a fairly steady, but not sharp, increase in reduction rate with temperature. Similar data for iron-catalyzed reductions were obtained from Experiments 3, 12, and 14; they are presented in Table VII and Figure 6.

TABLE VIII

Effect of Temperature on the
Iron-Catalyzed Reduction Rate

Temperature (°C)	Rate (%/hr)
600	17.5
650	25.0
700	38.1

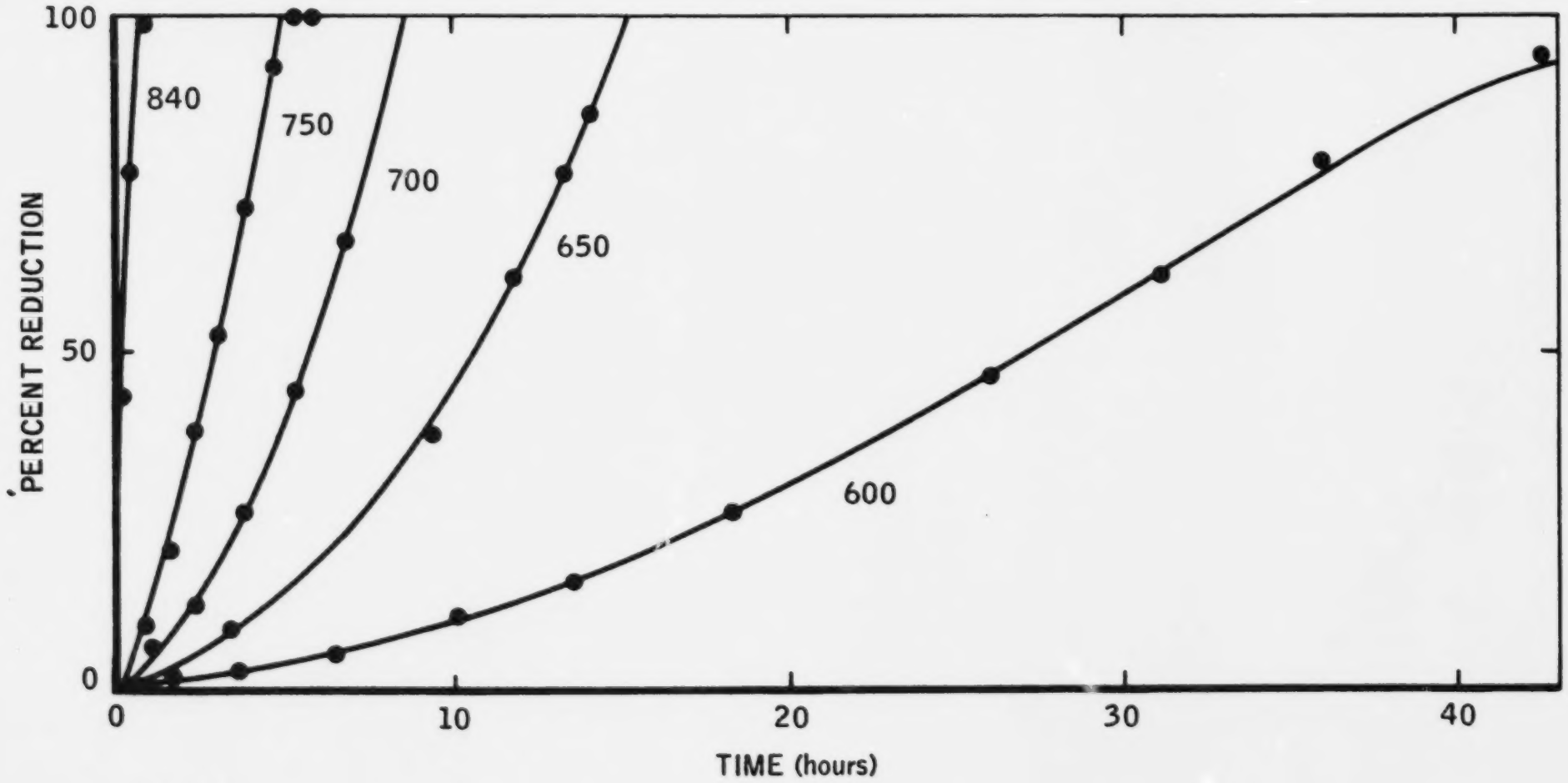

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Figure 5. Effect of Temperature on the Uncatalyzed Reduction Rate of Sulfate with Hydrogen

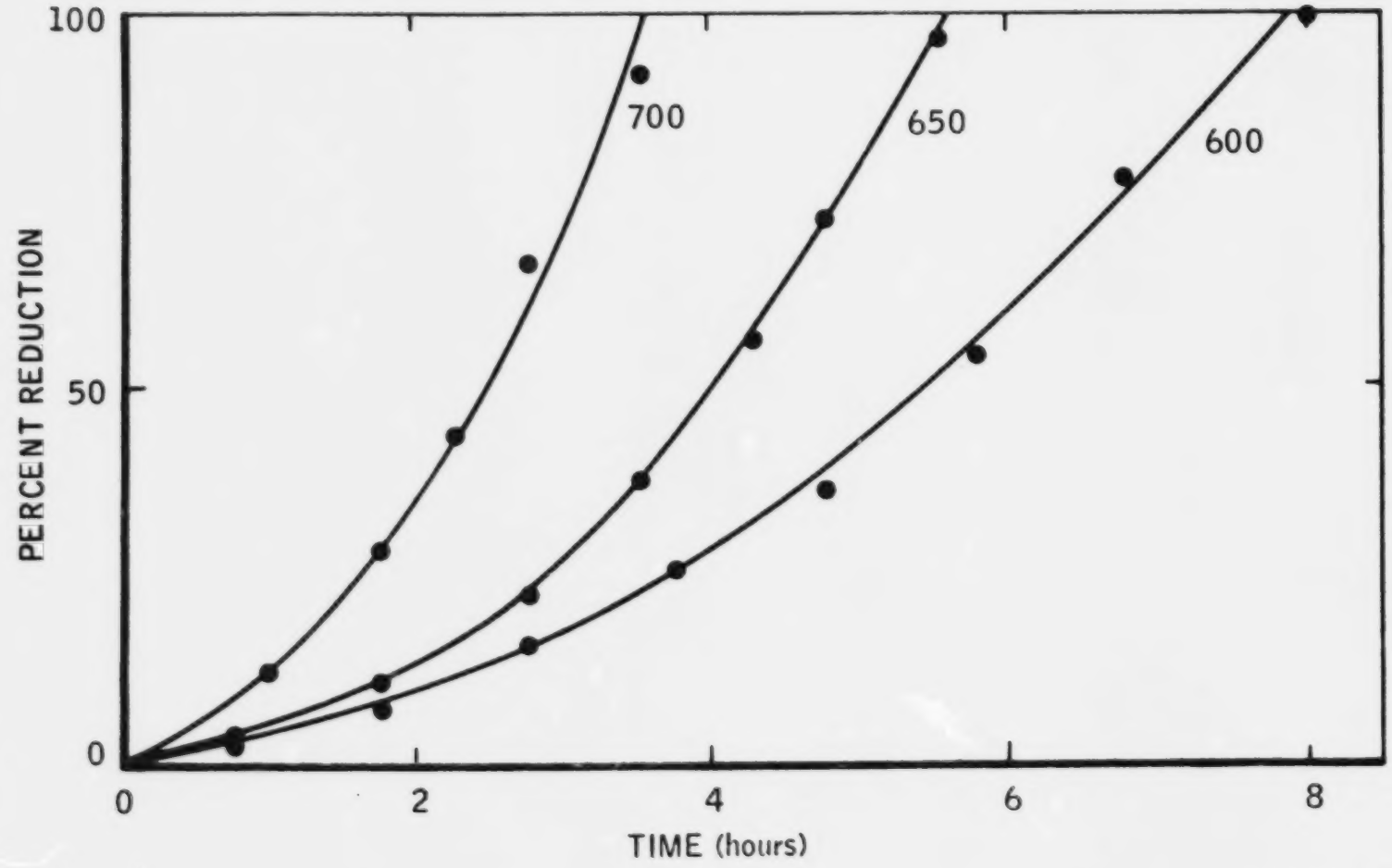

Figure 6. Effect of Temperature on the Iron-Catalyzed Reduction Rate of Sulfate with Hydrogen

In these tests the rate of increase was only about a factor of two for each 100°C temperature increase, while for the uncatalyzed tests, a factor of about four was observed. This result was not surprising since the iron undoubtedly lowered the activation energy of the reaction, thus making it less sensitive to temperature change.

3. Iron Catalysis

The comparitively high activity of iron as a reduction catalyst prompted two separate investigations in addition to the temperature study discussed previously: (1) the use of various chemical compounds containing iron as catalysts and (2) the effect of various concentrations of iron on the reduction rate. Three separate iron compounds (FeS, $FeSO_4$, Fe_2O_3), and elemental iron (Experiments 5, 3, 43, and 4, respectively) were employed as catalysts. The average reduction rate observed with each of these species is compared . . Table IX and Figure 7.

Table IX

Iron Catalysis

Form	Rate (%/hr)
FeS	19.4
$FeSO_4$	17.2
Fe_2O_3	15.6
Fe	12.8
Control	2.9

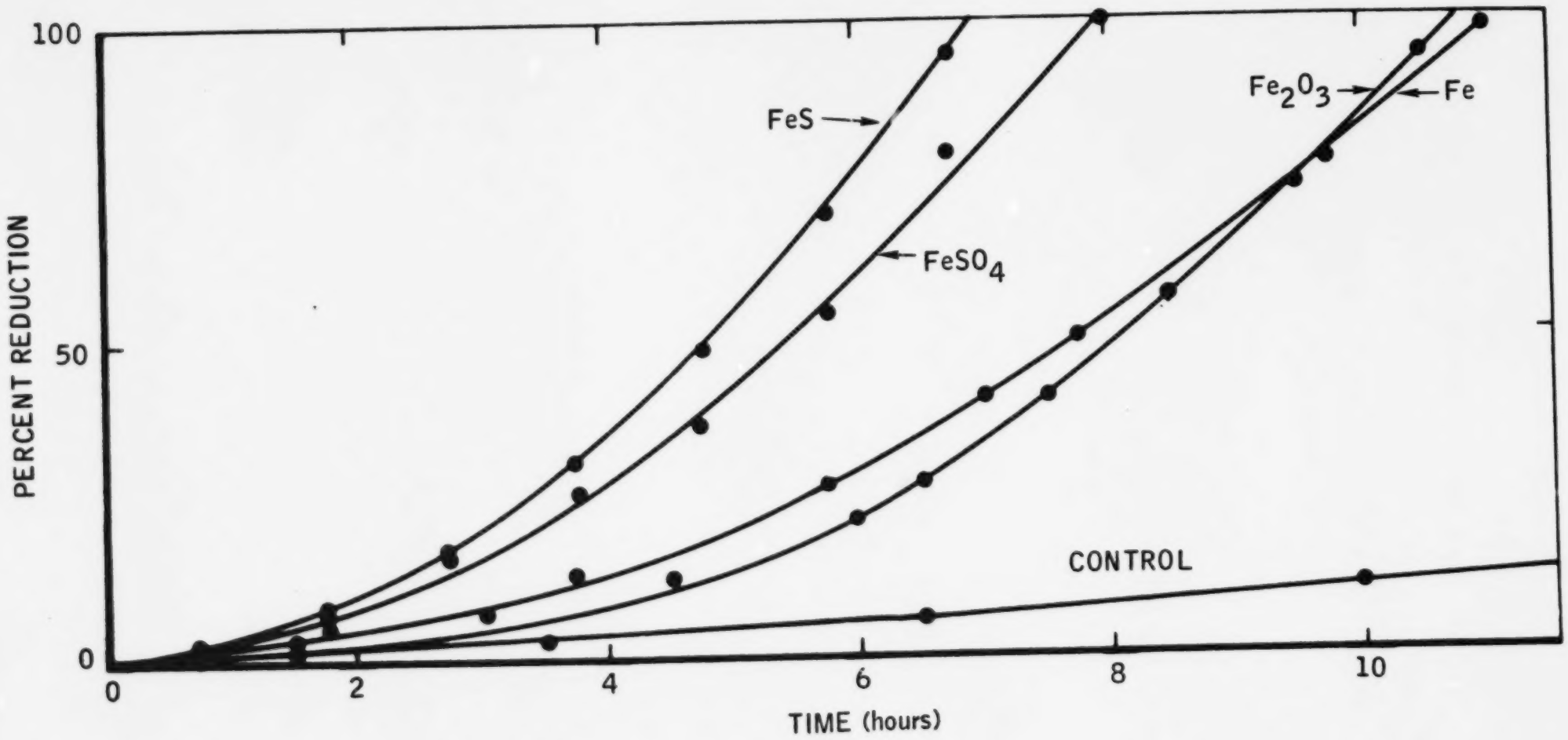

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Figure 7. Reduction of Sulfate with Hydrogen at 600°C using Various Iron Compounds as Catalysts

Although the length of the initial slow period (the induction time) changes with the use of different forms of iron, the actual rates vary only 40%. The difference between the control and the average rate with iron catalysts is 560%. The differences among the rates for the various iron compounds are probably attributable to the presence of sulfide (in the case of FeS and $FeSO_4$, the latter of which decomposes forming sulfide), and may also result from the rate at which the iron compound changes into the most stable form (and apparently the most active form) for the existing conditions.

To test the effect of iron concentration on the rate of reduction, iron concentrations of 0.01%, 0.09%, 0.23%, 1.3%, 2.4%, 4.8%, and 9.6% were employed as catalysts at 650 °C in Experiments 61, 63, 60, 24, 3, 21, and 66, respectively. The effect of the different amounts of iron is presented in Table X and Figure 8.

Table X

Catalytic Activity of
Varying Concentrations of $FeSO_4$

Concentration of Fe (wt%)	Reduction Rate (%/hr)
0.01	8.5
0.09	8.1
0.23	13.8
1.3	23.6
2.4	24.8
4.8	30.3

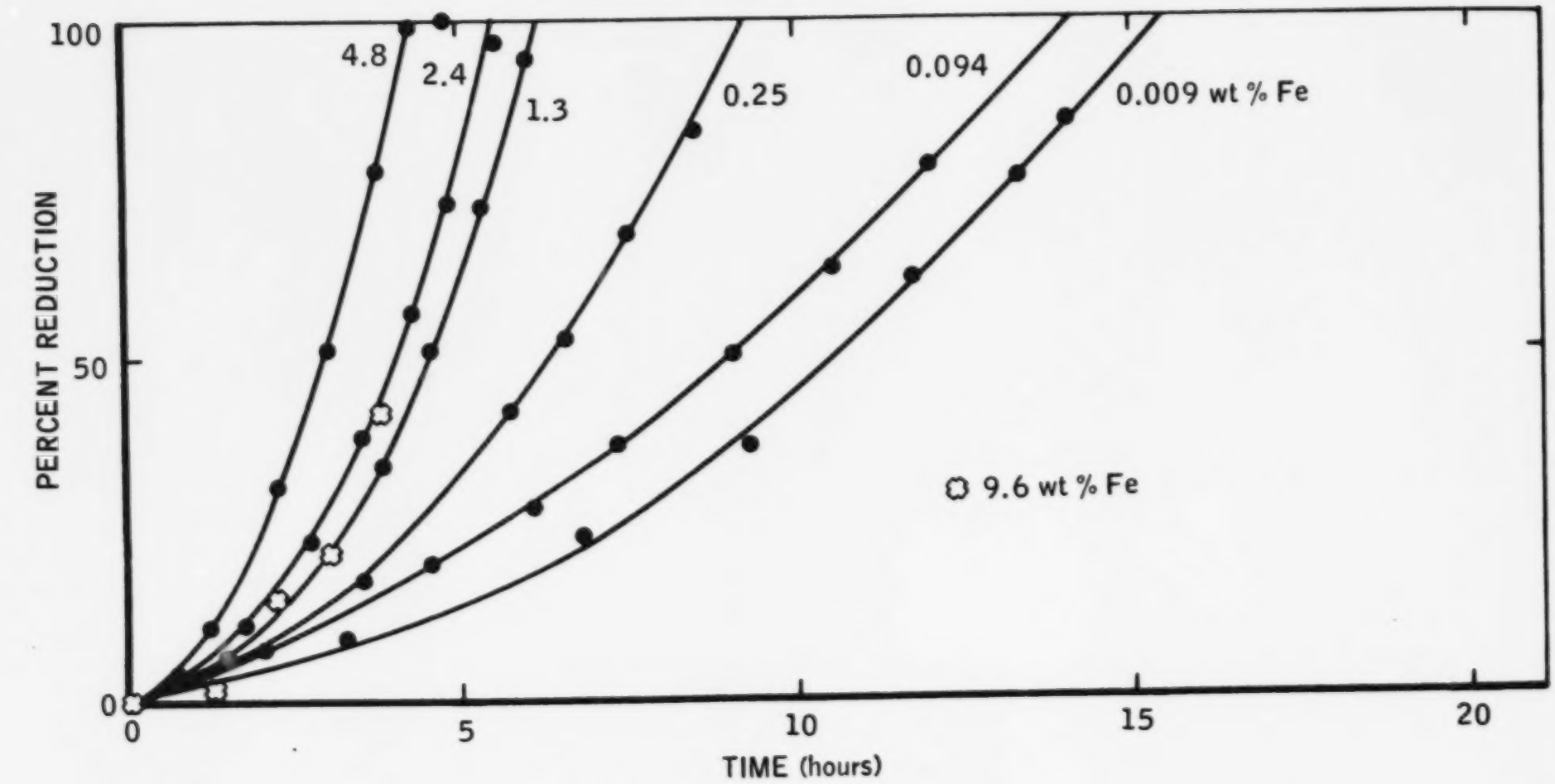

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Figure 8. Effect of Iron Concentration on the Reduction of Sulfate at 650°C using Hydrogen

Changing the iron concentration several orders of magnitude did not change the reduction rate correspondingly. It is important to note that the presence of 2.4% iron enhances the rate by a factor of less than three (compared to the control) at 650 °C, while at 600 °C 2.4% iron changes the rate by a factor of six (note Tables VII and VIII). Thus, iron is considerably more important at the lower anticipated reduction process temperatures.

4. Sulfide Catalysis

The literature review, the shape of the reduction vs. time curves, and preliminary results (3) all indicated that the reaction was autocatalytic as a result of sulfide catalysis. To investigate this effect a test was carried out at 650°C using a melt initially containing 22.5% alkali sulfide (Expt. 26) and compared with a test using no initial sulfide (Expt. 12). The results of these tests are shown in Table XI and Figure 9.

Table XI

Sulfide Catalysis

Initial Sulfide Concentration (wt%)	Reduction Rate (%/hr)
0	25.0
22.5	37.0

Figure 9 demonstrates that the slow initial rate was completely eliminated, thus confirming the hypothesis that the reaction is autocatalytic in sulfide. However, the average reduction rate of the

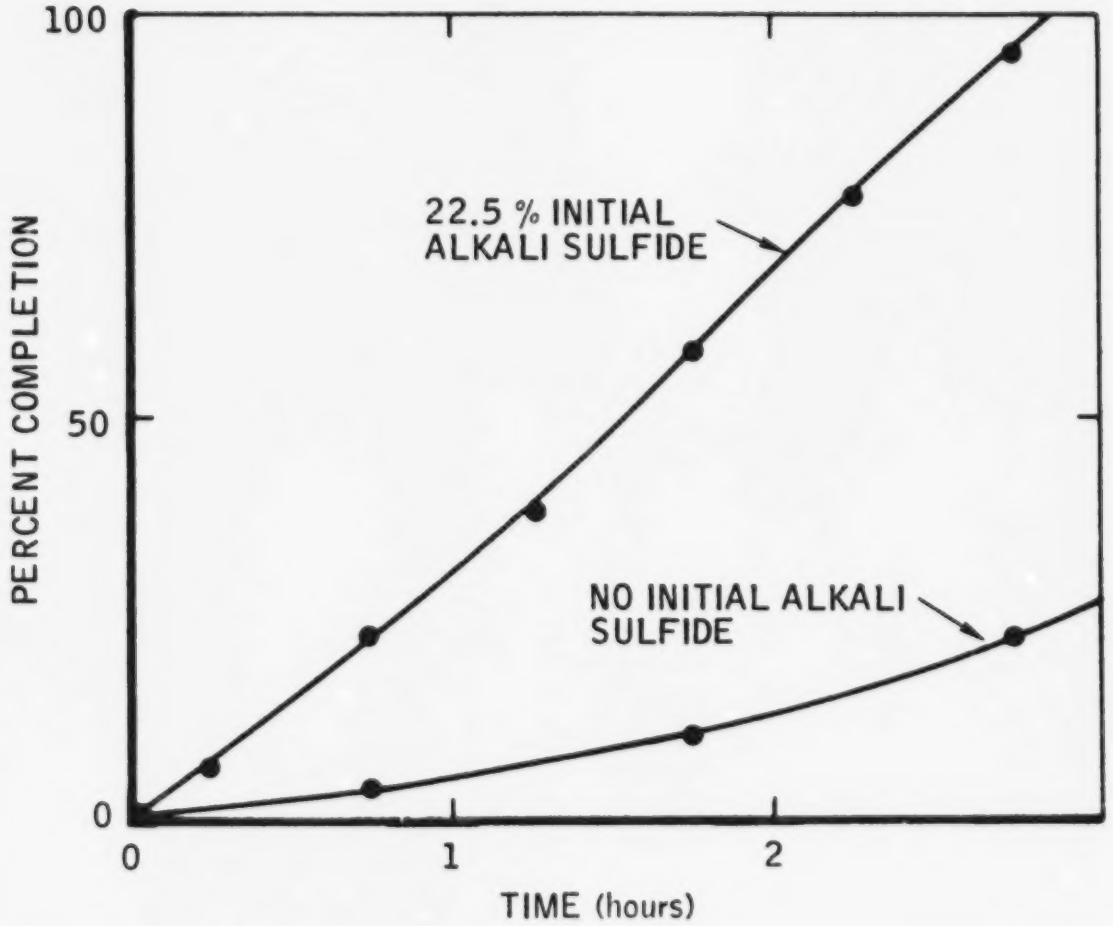

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Figure 9. Effect of Sulfide on the Rate of Reduction of Sulfate at 650°C

two tests is not too different, suggesting that the presence of sulfide at the onset eliminates the induction period but does not significantly increase the overall rate, since sulfide is the product of the reaction.

5. Effect of the Pressure

The effect of increasing the concentration of hydrogen molecules in the gas phase (i.e., pressure) was investigated in Experiments 17, 28, 29, 30, 31, 32, and 33. Experiment 17 was done at five atmospheres and at a flow rate of 1.4 ℓ/min (ambient conditions) of hydrogen. The rate of reduction was considerably slower than in the one atmosphere test (Expt. 3) done under otherwise identical conditions. These results suggested that the resulting decrease in agitation and surface contact between the liquid and gas due to lower gas volumes at the higher pressure was more important than the increase in pressure. Thus, Experiments 28-33 were designed to eliminate the variation in contact and agitation. This was done by keeping a constant volume throughput at all pressures employed. At pressures below one atmosphere, helium was mixed with hydrogen in the desired proportions; at pressures above one atmosphere the ambient flow rate was proportionately increased. The experiments were carried out at 600°C using both sulfide and iron catalysts. The results of these tests are presented in Table XII and Figure 10.

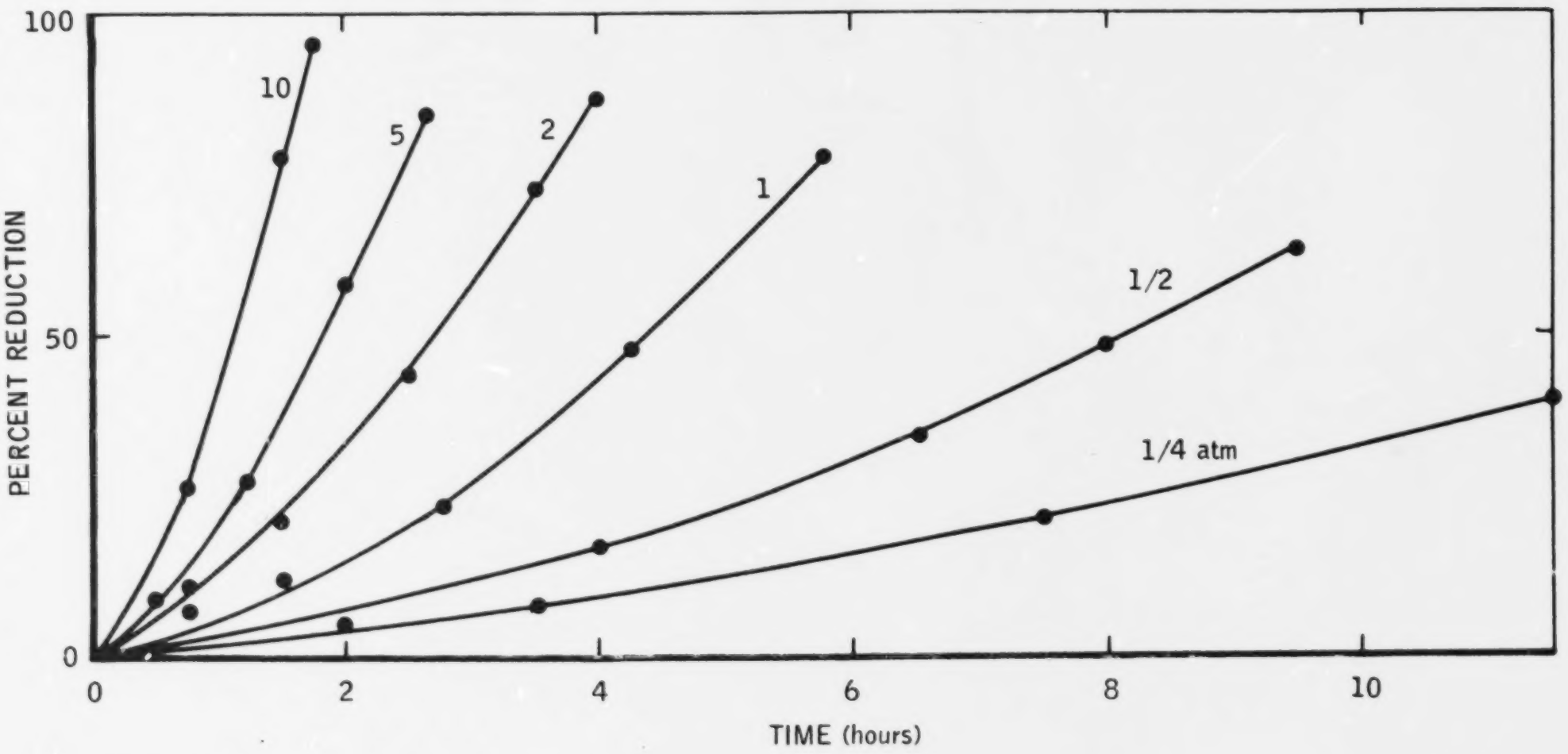

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Figure 10. Effect of Hydrogen Pressure on the Rate of Reduction of Sulfate at 600°C

Table XII

Effect of Hydrogen Pressure on Reduction Rate

Pressure (atm)	Reduction Rate (%/hr)
1/4	(6.0)
1/2	10.0
1	17.0
2	29.9
5	42.4
10	68.5

( ) Estimate based upon incomplete reduction data

These results show that the rate increases by about a factor of 1.6 for each two-fold increase in hydrogen concentration or pressure.

In conjunction with the pressure tests, two tests were done using water as opposed to helium to dilute the hydrogen. These tests (Experiments 19 and 53) were done to determine if water had any effect (e.g. cause a reversal of the reduction reaction) other than to dilute the hydrogen. The tests were done at 650°C. with both 0.4 and 0.7 atm water vapor pressure; the first is reported in Table XIII and Figure 11, along with a test (Expt. 12) using no water at otherwise identical conditions.

Table XIII

Effect of Water Vapor on Reduction Rate

Water Pressure (atm)	Hydrogen Pressure (atm)	Reduction Rate (%/hr)
0	1.0	25.0
0.4	0.6	16.4

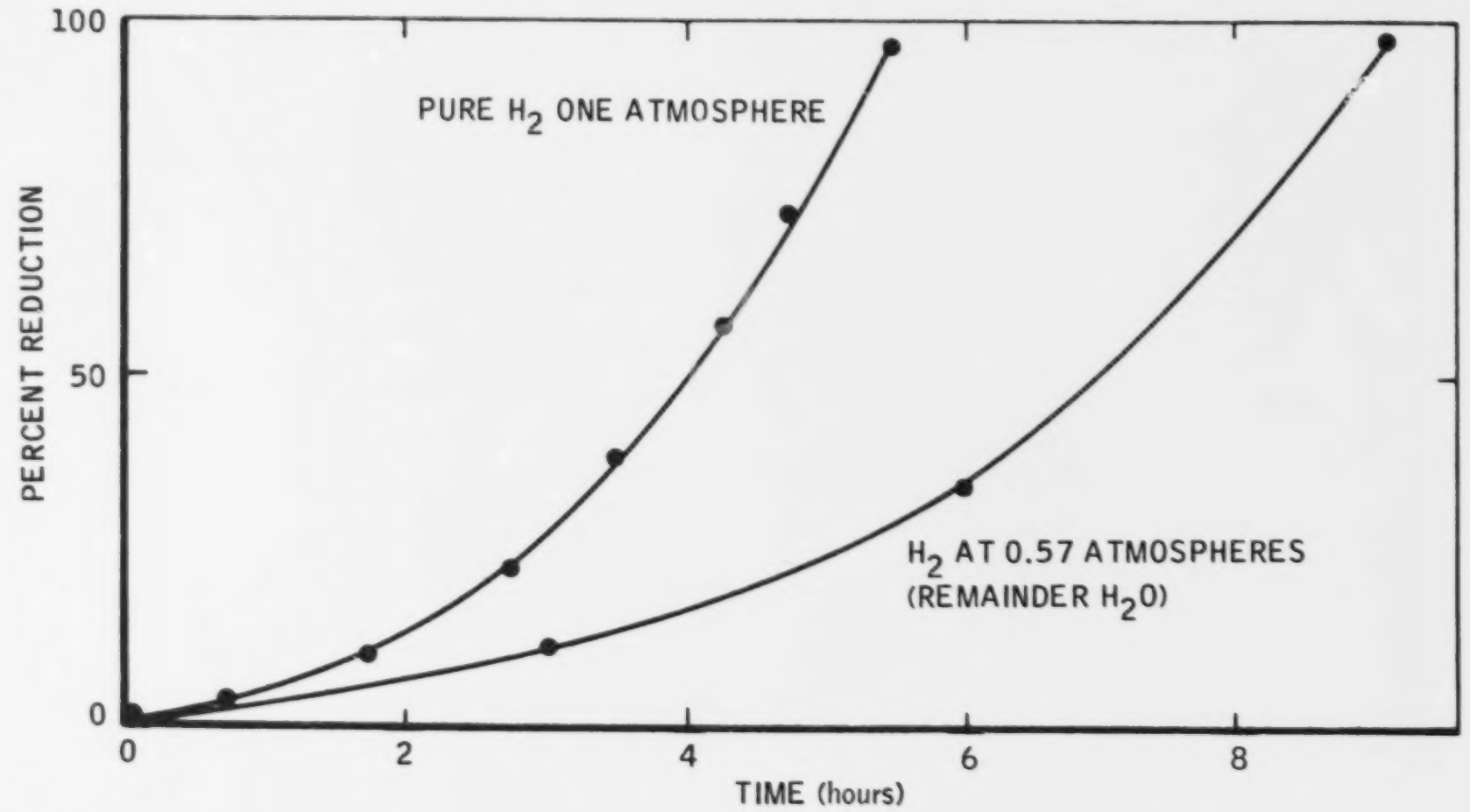

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Figure 11. Effect of Water Vapor on the Reduction of Sulfate with Hydrogen at 650°C

The reduction rate with 0.6 atm hydrogen (0.4 atm H_2O) was 34% slower than with pure hydrogen. Based upon the pressure studies one would expect a rate decrease of 30% if water vapor acted only as a diluent. This close agreement points to the conclusion that water vapor simply acts as an inert diluent in the reduction of sulfate with hydrogen.

The test using 0.7 atm water vapor was not followed up with an identical test using no water; however, semi-quantitative results indicated the same conclusion as mentioned above.

6. Effect of Contact

The effect of mass transfer upon reaction rate was investigated by changing the flow rate of hydrogen from 1.4 (Expt. 12) to 2.9 ℓ/min (Expt. 18) and by comparing a rotating packed bomb test (Expt. 25) with a bubble contactor test (Expt. 3). The first two tests are compared in Table XIV and Figure 12.

TABLE XIV

Effect of Flow Rate
on Reduction Rate

Flow Rate (ℓ/min.)	Reduction Rate (%/hr.)
1.4	25.3
2.9	35.0

The increased reduction rate with flow rate could be caused by at least two phenomena, one physical and one chemical. First, increased flow could result in increased mass transfer through increased agitation and surface area. Secondly, if the conversion is controlled by thermodynamics, as opposed to kinetic factors, the increased amount of hydrogen

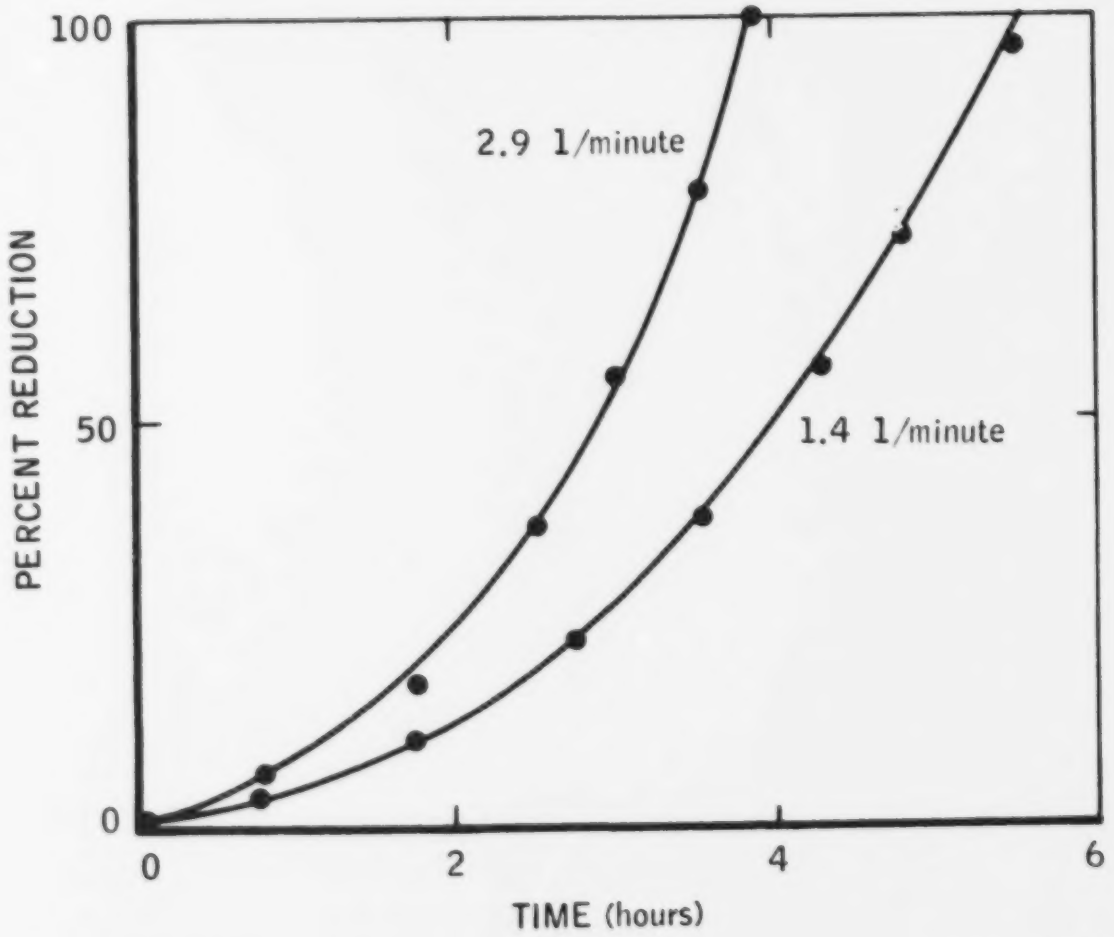

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Figure 12. Effect of Flow Rate on the Rate of Reduction of Sulfate with Hydrogen at 650°C

would shift the reaction further towards completion. However, thermodynamic calculations, the autocatalytic behavior of the reaction, and the effect of water in the reducing gas stream all indicate that the reaction is not thermodynamically controlled, thus suggesting that flow rate affects the reaction through surface area and agitation.

To further study the effect of surface area, a test was performed in which the melt was contacted with the hydrogen in a rotating packed-bed reactor. This reactor was a graphite tube (10 in. by 1 5/8 in. I.D.) filled with 1/4 in. graphite raschig rings. The tube was rotated in the horizontal position at about 11 rpm.

Table XV and Figure 13 compare tests using the bubble contactor and the rotating reactor under similar conditions, but with different amounts of starting material.

Table XV

Reactor Design and Reduction Rate

Design	Reduction Rate (%/hr)
Bubble Reactor	17.5
Packed Reactor	53.6 *

* Based upon water evolution

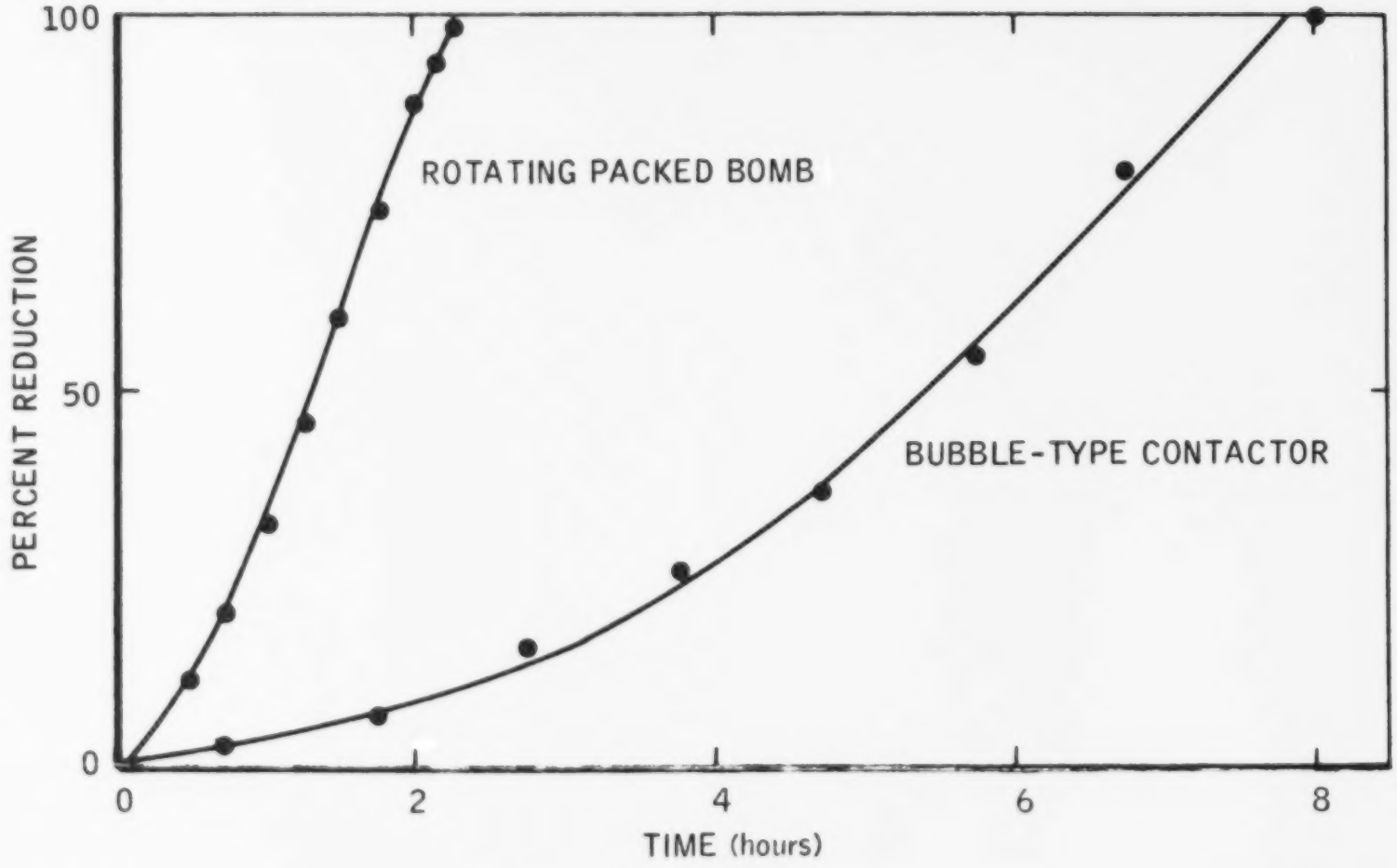

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Figure 13. Comparison of Packed Reactor and Bubble Contactor for the Reduction of Sulfate with Hydrogen at 600°C

These tests again demonstrate that greater surface leads to faster reduction. However, it should be pointed out that the absolute rate (i.e. moles/hr) varies only by a factor of 25% between the two tests. This results from the fact that the initial amounts of sulfate present in the two tests were quite different.

B. CARBON MONOXIDE REDUCTIONS

1. Catalysis

Since both tin and iron were found to be effective catalysts for hydrogen reductions, they were tested at 700°C, (Expts. 51 and 46-C) as possible catalysts in carbon monoxide reductions. A comparison of these two tests and a control (Expt 45-C) is presented in Table XVI and Figure 14.

Table XVI

Effect of Iron and

Tin on the Reduction Rate

Catalyst	Reduction Rate (%/hr)
None	18.2
$SnSO_4$	7.1
$FeSO_4$	7.1

These results indicate that both tin and iron similarly inhibited the overall reduction with carbon monoxide. Both curves were nearly linear, with the reduction going faster than the control at first, but eventually going slower because there was no rapid increase of rate with time as there was for the control.

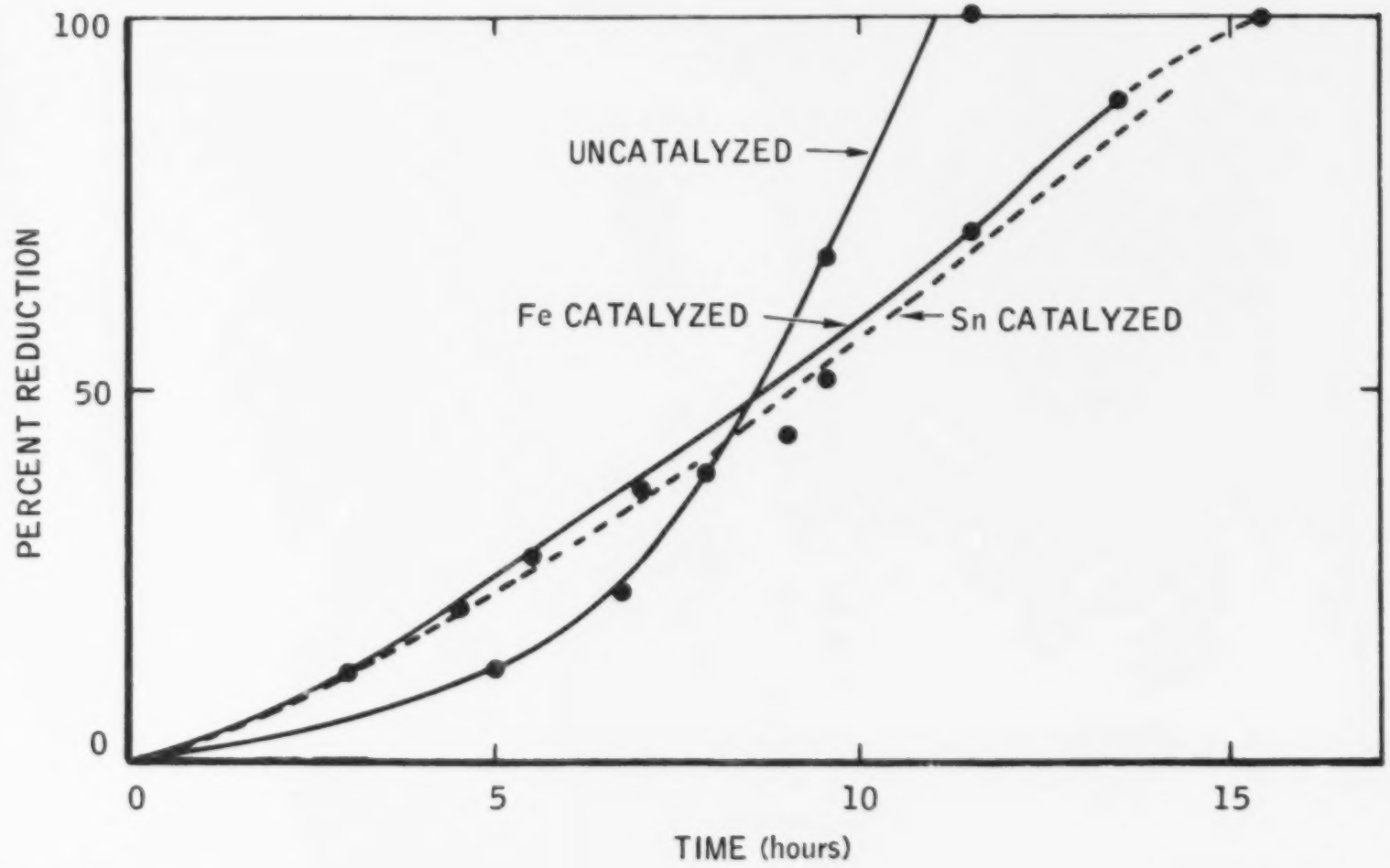

Figure 14. Reduction of Sulfate with Carbon Monoxide at 700°C

An iron catalyzed reduction test using 10% carbon dioxide and 90% hydrogen (Expt. 58) indicated that carbon dioxide (a product of the carbon monoxide reduction) inhibits the reduction rate, probably by tying up the iron and sulfide in some catalytically inactive (and possibly more insoluble) form. In the experiment, the reduction rate was decreased considerably more than would be expected from effects due only to dilution of the hydrogen by an inert gas. The results shown in Table XVII and Figure 15, compare the rate using the hydrogen-carbon dioxide mixture with that using pure hydrogen (Expt. 14).

Table XVII

Reducing with Hydrogen/Carbon Dioxide Mixture

Reducing Gas	Reduction Rate (%/hr)
H_2 (100%)	34.5
$H2/CO_2$(9:1)	22.7

It is seen that a gas mixture containing only 10% carbon dioxide reduces the rate by 34%, whereas less than a 10% reduction would be expected if carbon dioxide were inert.

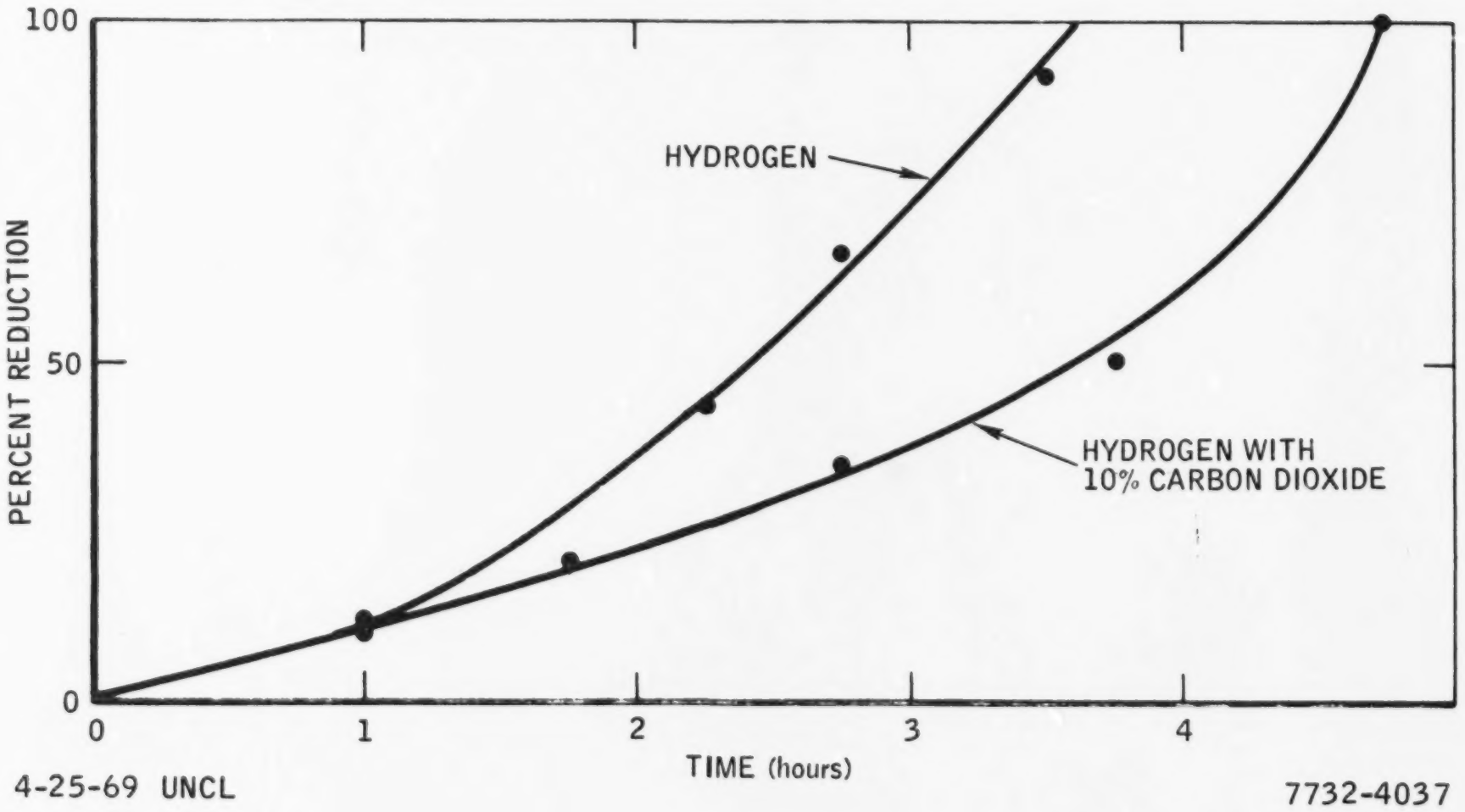

Figure 15. Effect of Carbon Dioxide on the Iron-Catalyzed Reduction Rate of Sulfate Using Hydrogen at 700°C

Table XVIII and Fimure 16 show that sulfide is a catalyst for carbon monoxide reductions (Expt. 45-C and 47-C).

Table XVIII

Sulfide Catalysis

Catalyst	Reduction Rate (%/hr)
None	18.2
H_2S	33.3
$FeSO_4$	7.1
$H_2S/FeSO_4$	11.1

Here again, iron, even in the presence of sulfide, was found to inhibit the reduction rate (Expt. 48-C).

2. Temperature Studies

Uncatalyzed reductions were studied as a function of temperature. Tests were carried out at 600, 700, and 840°C (Expts. 44-C, 45C and 54, respectively) and the results are compared in Table XIX.

Table XIX

Effect of Temperature

on Carbon Monoxide Reduction Rate

Temperature (°C)	Reduction Rate (%/hr) *
600	0.71
700	7.9
840	12.0

* Between 10 and 40% completion: 75% completion was not attained by the conclusion of the 840°C test.

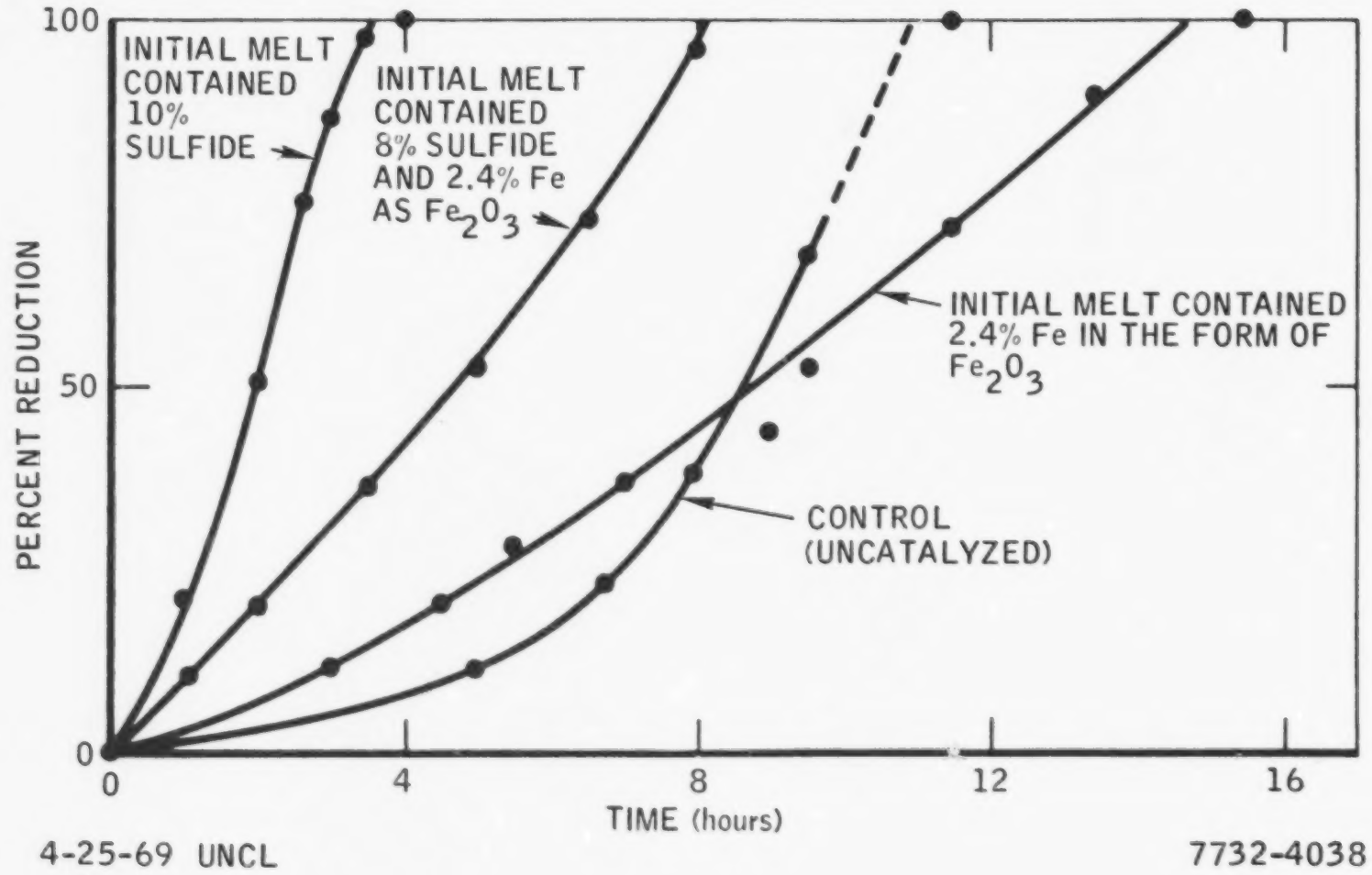

Figure 16. Effect of Sulfide and Iron on the Rate of Reduction of Sulfate with Carbon Monoxide at 700°C

As the temperature was increased from 600 to 700°C, the reduction rate went up more than an order of magnitude. However, between 700 and 840°C the rate less than doubled. These results are quite different than the steady increase in rate observed with hydrogen, and they are quite difficult to interpret. Thermodynamics calculations, however, show that the free energy of the reduction reaction with carbon monoxide decreases with increasing temperature due to increased stability of carbon monoxide as compared to carbon dioxide. However, at 840°C, the free energies of the carbon monoxide and hydrogen reductions are identical (See Table II).

3. Pressure

The effects of pressure using carbon monoxide at 1/2 (Expt. 55) and 1 atm (Expt. 47-C) were studied at 700°C. The results of these tests are given in Table XX and Figure 17.

Table XX

Effect of Pressure

on Carbon Monoxide Reductions

Pressure (atm)	Reduction Rate (%/hr)
1/2	14.8
1	33.3

These results show that at one atm the reduction rate with carbon monoxide is 2.25 times faster than that at 1/2 atm. The average rate change with hydrogen was found to be 1.56 when the pressure was changed by a factor of two.

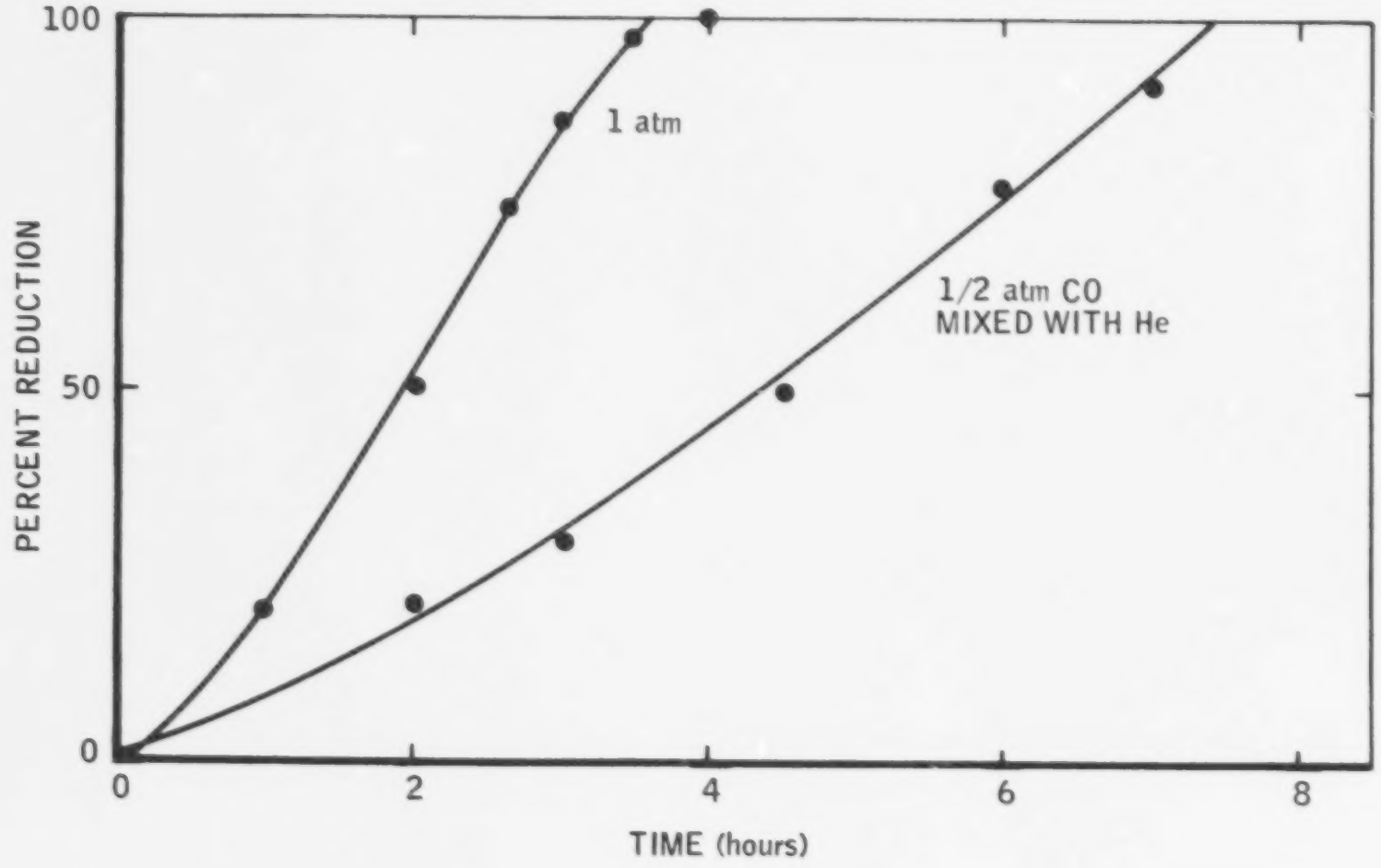

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Figure 17. Effect of Pressure on the Rate of Reduction of Sulfate using Carbon Monoxide at 700°C

The rate change between one-half and one atm for hydrogen was 1.7. These results are in qualitative agreement with those obtained by Grantham and Weredy (20) which indicated that carbon monoxide reductions were more pressure sensitive than hydrogen reductions.

C. OTHER REDUCING AGENTS

1. Producer Gas

A simulated producer gas mixture containing nominally an equal amount of carbon monoxide and hydrogen was used to reduce the sulfate at 700°C (Expt. 49). Figure 18 shows the results of this experiment and demonstrates that hydrogen is approximately twice as effective as carbon monoxide; however, tests using pure hydrogen and carbon monoxide (Expts. 6 and 45-C) demonstrated that the two were about equally effective at 700°C (Table VII and XVIII). This discrepancy appears to result from the fact that hydrogen reductions were much less pressure sensitive than those done with carbon monoxide. Therefore, a lowering of the pressure to one-half atmosphere for each gas, as was the case in the producer gas reduction, caused the rate to drop off more with carbon monoxide than with hydrogen.

2. Fluidized Coke

Fluidized coke, which is a petroleum by-product, was used as a reducing agent at 600°C (Expt. 59), 700°C (Expt. 56), and 800°C, (Expt. 62), and at 700°C and 800°C in the presence of iron (Expts. 57 and 68).

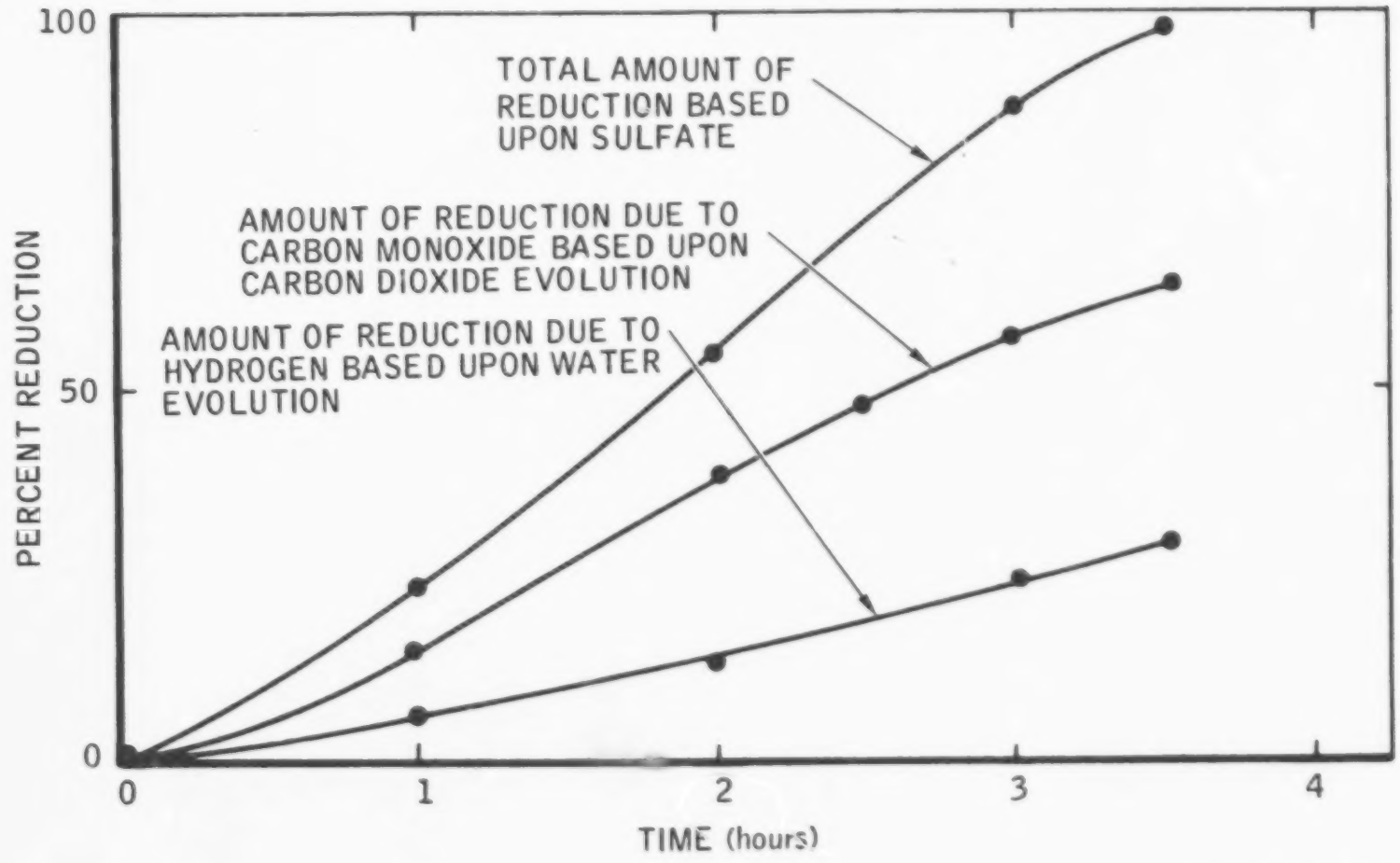

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Figure 18. Reduction of Sulfate Using Equal Volumes of Hydrogen and Carbon Monoxide at 700°C

In each of these tests 2-1/2 times the stoichometric amount of coke was used. The results are presented in Table XXI and compared with the hydrogen and carbon monoxide reductions in Figure 19 and Table XXII.

Table XXI

Reductions with Fluidized Coke

Conditions	Reduction Rate (%/hr)
600°C	1.1[a]
700°C	35.5
700°C with Fe	52.6
800°C	200
800°C with Fe[b]	430

(a) Based upon the first 31.5% reduced (28-1/2 hours)

(b) Mechanical agitation, as opposed to agitation by means of a purge gas, was employed in this experiment.

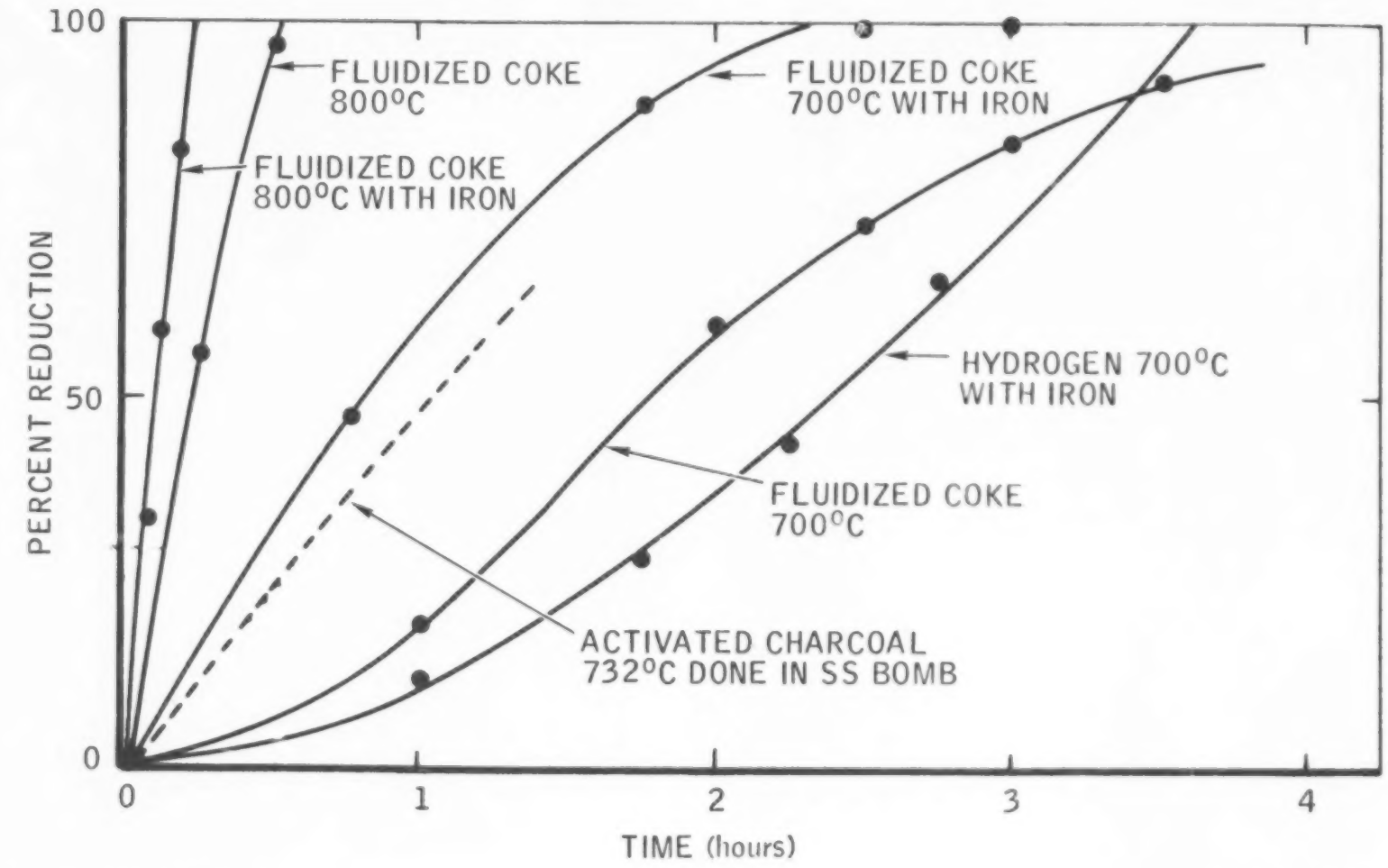

Figure 19. Comparison of Reducing Agents under Various Conditions for the Reduction of Sulfate

Table XXII

A Comparison of Reducing Agents

Reducing Agent	Catalyst	Temperature (°C)	Rate (%/hr)
Hydrogen	None	700	14.8
Carbon monoxide	None	700	18.2
Fluidized coke	None	700	34.7
Hydrogen	Fe	700	38.1
Carbon monoxide	Fe	700	7.1
Fluidized coke	Fe	700	52.1
Hydrogen	none	840	100
Carbon monoxide	none	840	28
Fluidized coke	none	800	200

The reaction rate change with temperature was similar to that in carbon monoxide reductions where between 600 and 700°C there was a sharp increase, and between 700 and 800°C the increase was considerably smaller. The effect of iron, however, was like that in hydrogen reductions where the addition of iron markedly increased the rate. In addition, with fluidized coke, iron not only acted as a catalyst, but also appeared to be responsible for forcing the reaction to completion in that the carbon monoxide concentration was considerably smaller in the iron-catalyzed test. These results of the exit-gas analysis are given in Table XXIII.

Table XXIII

Exit Gas Analysis for
Fluidized Coke Reductions

Test	Time (min)	CO(%)*	CO_2(%)*
700°C no catalyst	14	5.1	14.9
	40	3.0	20.1
	97	1.5	37.5
	162	2.1	31.2
700°C $FeSO_4$ catalyst	24	0.63	38.2
	35	0.45	47.9
	102	1.02	30.6
	156	1.21	16.7
800°C no catalyst	5	19.1	41.6
	12	12.3	77.8
	22	10.0	66.7
Blank with $FeSO_4$ - 730°C(no coke)	-	0.098	0.92
Blank with $FeSO_4$ - 790°C(Expt. 52)	-	0.51	2.30

*Remaining percentage was helium.

Since iron was found to inhibit the reduction of sulfate with carbon monoxide, it is likely, therefore, that in these tests iron catalyzes the reaction of coke with sulfate as opposed to the reaction of carbon monoxide, one of the products of the coke reaction, and sulfate.

The rates shown in Figure 19 and Table XXII should be compared carefully, since the reductions involve gases on the one hand and a solid on the other. The rate of reduction with hydrogen and/or carbon monoxide can be increased by changing any of several parameters (e.g. pressure and gas-liquid

contact area), while the rate with carbon probably cannot be significantly increased.

3. Tetralin

Tetralin (1,2,3,4-Tetrahydronapthalene) has been used for high-pressure, high-temperature hydrogenation reactions.(41) The labile hydrogens on the 1,2,3, and 4 positions participate in reductions forming the very stable product, napthalene. In general, the reductions are done at high pressure where tetralin (B.P. 207°C) is in the liquid phase. Tetralin in the vapor phase was tried as a reducing agent at 450, 500 and 600°C (Expt. 37). At 600°C ferrous sulfate was utilized as a possible catalyst. Under all conditions employed, no appreciable reduction was observed. In addition, gas chromatographic results showed almost no decomposition of the tetralin.

D. DISPROPORTIONATION AND REDUCTION OF SULFITE

Alkali metal sulfites are the actual products of the absorption step in the Molten Carbonate Process; however, these compounds disproportionate into sulfide and sulfate and are also oxidized by air to sulfate. This is the reason the emphasis in the reduction work concentrated on reducing sulfate as opposed to sulfite. In order to provide more accurate and complete information, and also to gain some insight into the reduction mechanism, a study of the disproportionation and reduction of sulfite was carried out.

1. Effect of Temperature

The disproportionation of sulfite was investigated at 500, 550 and 600°C in Expts. 34, 38 and 39, respectively. The results of these tests are given in Table XXIV and a typical disporportionation vs. time curve is given in Figure 20.

Table XXIV

Effect of Temperature
on the Disproportionation Half-life

Temperature (°C)	Half-life (hrs.)
500	9.9
550	2.9
600	0.38

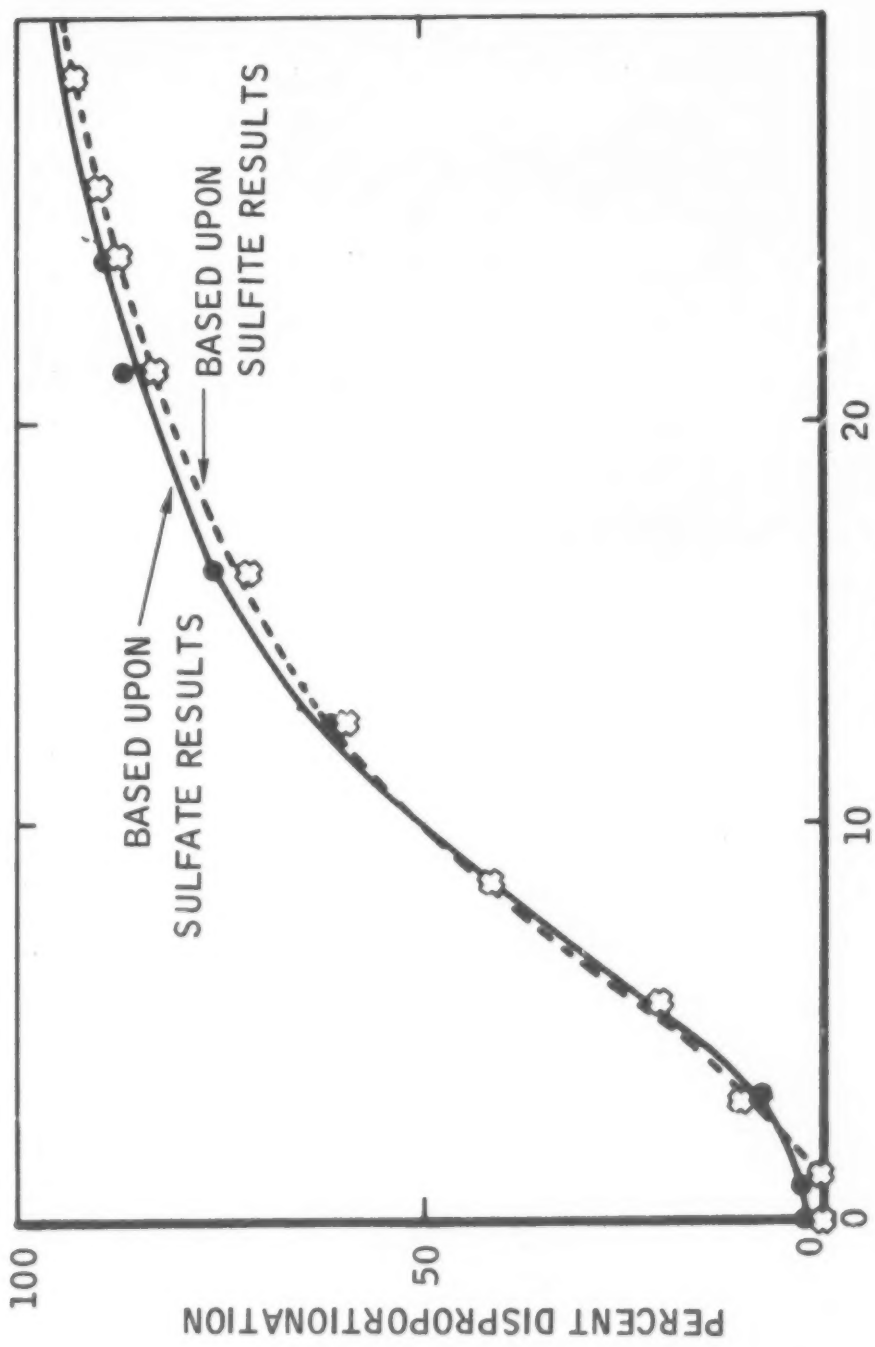

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Figure 20. Disproportionation of Sulfite at 500°C

It is important to note that the half-life decreased by a factor of 3.4 between 500 and 550°C while between 550 and 600°C the factor was 7.6. As a result, a plot of half-life vs. reciprocal absolute temperature was nonlinear suggesting that one result may be incorrect (possibly due to the catalytic effect of varying small amounts of iron leached from the graphite crucible).

The shape of the curve in Figure 20 indicated a reaction order of about one. This was checked with a first-order plot of the log of the sulfite concentration vs. time and also a plot of the log of the final sulfate concentration minus the instantaneous sulfate content vs. time. This plot presented in Figure 21, indicate the reaction is first-order in agreement with previously published data (30). Thus, the slow step in the reaction involves the decomposition of a single molecule of sulfite as opposed to a bimolecular reaction where two sulfite molecules would interact.

2. Effect of Iron Oxide

The effect of ferric oxide (Fe_2O_3) on the rate of disproportionation was studied at 525°C (Expt. 41). The results of this test are shown in Figure 22. The observed half-life was about 25 minutes, which is about ten times faster than the uncatalyzed (no Fe_2O_3 present) rate at the same temperature. The linearity of the curve, after an initial rapid disproportionation, in Figure 22 indicates that the order of the reaction is zero. This suggests that sulfite may be rapidly changed into some other sulfur-containing compound in the presence of iron oxide. This other compound then slowly disproportionates in the rate-determining step.

3. The Reduction of Sulfite

Experiments 35 and 36 were carried out to study the reduction and, unavoidably, the simultaneous disproportionation of sulfite. One was done in the presence of ferric oxide (Expt 36) while the other (Expt. 35)

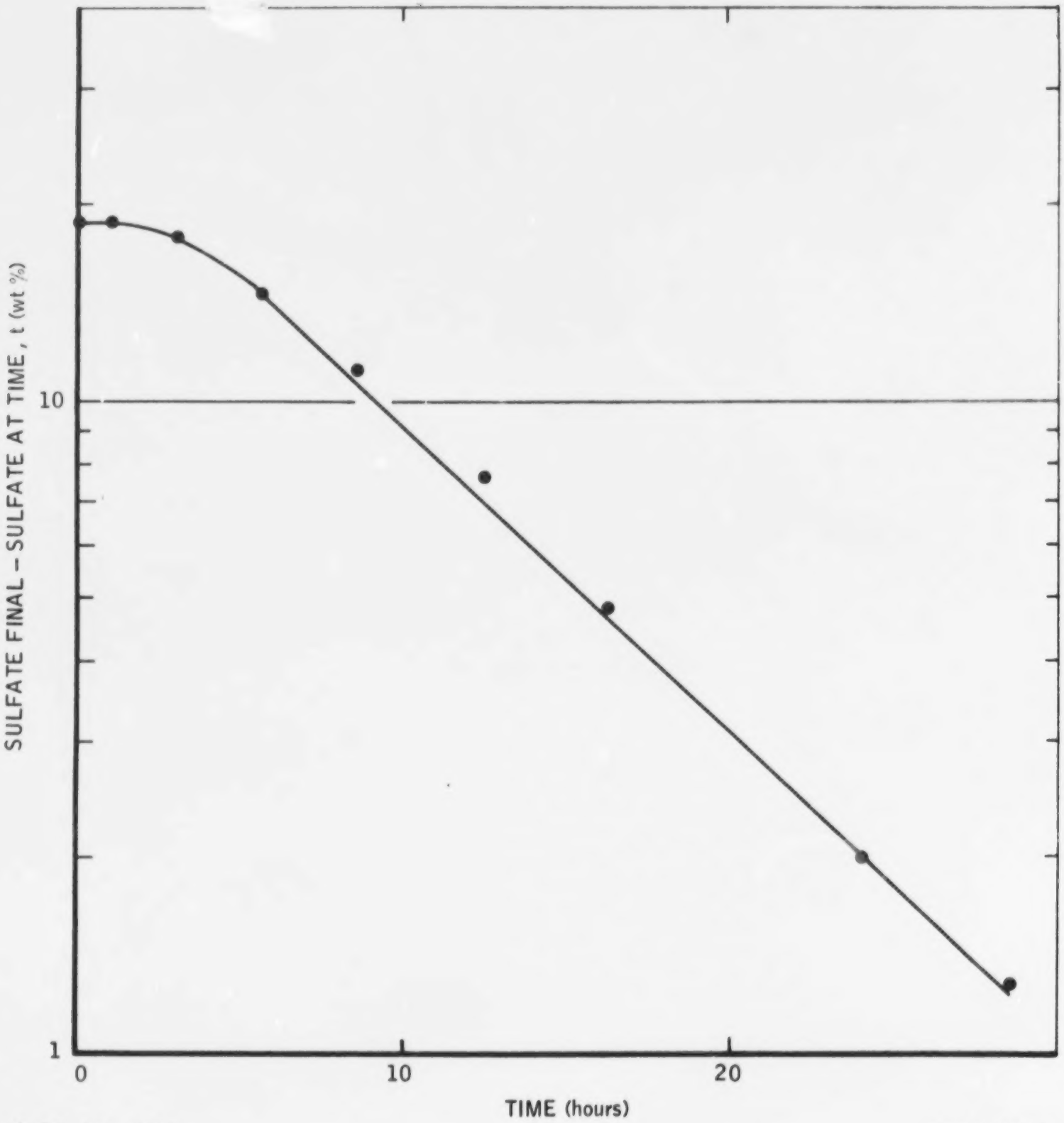

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Figure 21. Disproportionation of Sulfite in the Carbonate at 500°C

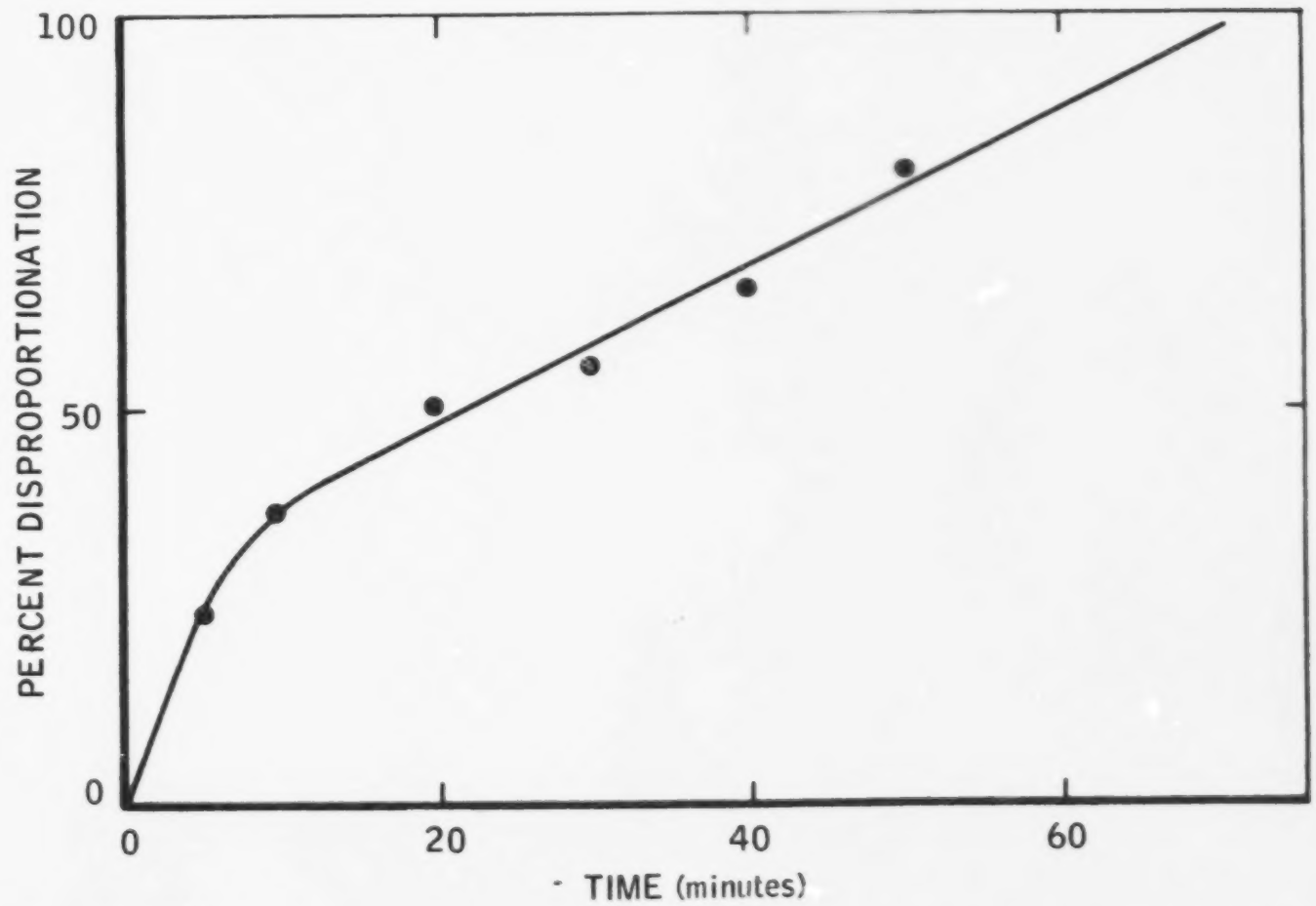

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Figure 22. Disproportionation of Sulfite in the Pressure of Iron Oxide at 525°C

was carried out without the presence of additional material other than the carbonate melt. The results of the uncatalyzed experiment are presented in Figure 23. The data show that the disproportionation rate was considerably faster than the reduction rate at sulfite concentrations greater than about 12%. In addition, the shape of the reduction curve strongly suggests a very small and possibly a zero order reaction with respect to sulfite. Furthermore, the increasing rate of reduction (even though the reactant concentration is rapidly decreasing) suggests autocatalysis. Finally, in the presence of ferric oxide, the disproportionation is catalyzed to a considerable extent while the reduction appears to be unaffected. However, the overall reduction rate was greatly diminished due to the decreased amount of sulfite caused by the rapid disproportionation. It should be pointed out that in contrast to these results, one Russian worker (15) found that the reduction was considerably faster than the disproportionation (in the solid phase); however, two others (35) demonstrated that the disproportionation was greatly accelerated by carbon during carbonaceous reductions of sulfite.

The reduction of sulfite was found to be considerably faster than that of sulfate. This is especially noted in the curves in Figure 23, where it can be seen that the reduction nearly ceased after the sulfite had completely reacted and only sulfate remained to be reduced. Based upon previous results at 600 and 700°C, the reduction rate for sulfate is projected to be about 0.6%/hr at 500°C, while the observed rate for sulfite at the same temperature was about 2.7%/hr (between 10-40% completion). In general, it appears that the reductions of sulfite and sulfate are quite similar except that the former is faster and is complicated by disproportionation.

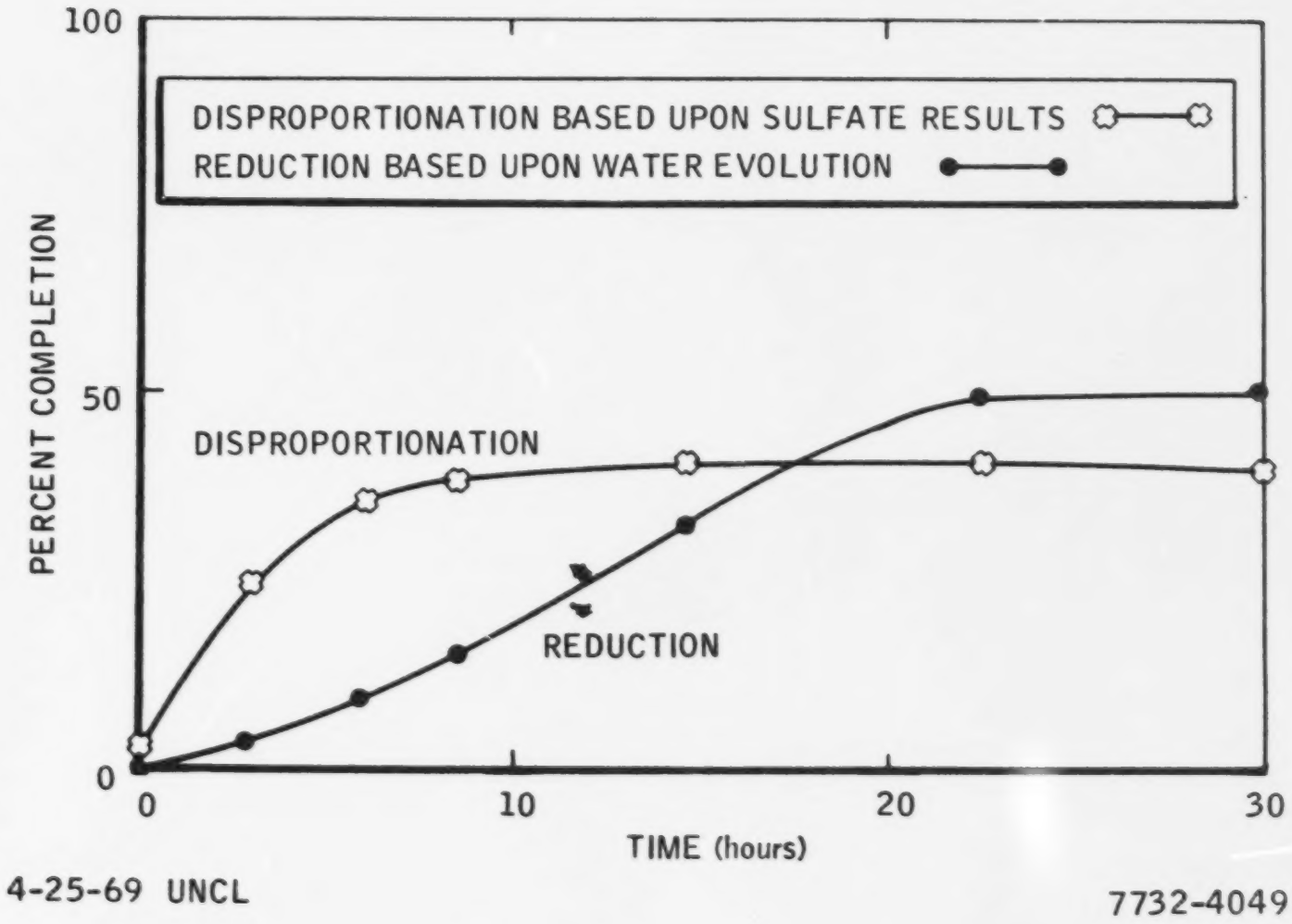

Figure 23. Simultaneous Disproportionation and Reduction (with Hydrogen) o. Sulfite in Carbonate Eutectic at 500°C

IV. ANALYSIS OF THE HYDROGEN REDUCTION DATA

Rational design of a chemical reactor requires a reaction rate expression which accounts for pertinent reaction variables. The rate expression aids in selection of a reactor type, design of the reactor, and specification of operating conditions. The data from batch reductions of sulfate, under varied conditions were analyzed to formulate a single rate expression.

The problems in extracting a single rate expression from batch data include isolating the independent variables which affect the rate, framing a realistic mathematical model relating the variables, and unraveling the intertwined effects of the several variables. As in a homogeneous reaction, the reaction rate in gas-liquid reduction depends upon the concentrations of chemical species and catalysts. Unlike a homogeneous reaction, the rate of the heterogeneous reduction is influenced by mass transfer variables such as bubble size, shape, and motion, and degree of liquid agitation.

In discussing the empirical approach to gas-liquid reactor design, Bridgewater and Carberry (4) explain, "In many industrial situations....the reaction mechanism may well be complex and it may be very hard to disentangle the diffusion and reaction effects in a meaningful and quantitative way." Kingsly and Bliss (28) studied the kinetics of hydrochlorination of lauryl alcohol, $ROH(l) + HCl(g) \rightarrow RCl(l) + H_2O(g)$, a reaction similar to the reduction of sulfate. Their detailed reaction rate expression which accounts for mass transfer and kinetics was

$$-\frac{d}{dt}[ROH] = K'[ROH]^{x_1}[HCl]^{x_2} \qquad (5)$$

$$K' = \left(x_3 + x_4[\text{catalyst}]\right)(G/V)^{x_5} \qquad (6)$$

(where brackets denote concentrations, x's are constants, and (G/V) is a gas-flow-rate to reactor-volume ratio). This expression enables the designer to assess various reactor networks and gives some insight into the reaction mechanism. It is important to recognize that the overall reaction rate constant, K′, includes reaction kinetics as well as mass transfer properties.

The need for an expression of this type (Equation 6) in designing the reduction reactor and the similarity between the hydrochlorination of lauryl alcohol and the reduction of sulfate led to the following analysis. The hypothesis underlying the data analysis is that the several effects are separable; that is, the overall rate expression is the product of several functions, each representing the effect of a single variable.

A. DETERMINATION OF THE REACTION ORDER WITH RESPECT TO SULFATE CONCENTRATION

The overall reaction rate expression associated with the gas-liquid reaction

$$M_2SO_4(l) + 4\ H_2(g) \xrightarrow{\text{catalyst}} M_2S(l) + 4\ H_2O(g) \qquad (7)$$

would be expected to be of the form

$$-\frac{d}{dt}[M_2SO_4] = K'\,[M_2SO_4]^{p}\,[H_2]^{m} \qquad (8)$$

where brackets denote concentrations, p and m are constants (i.e. the reaction order), and K′ is an overall reaction rate constant including effects of temperature, catalyst concentration, and mass transfer effects attributable to conditions such as impeller speed, bubble size, or gas flow rate. The reverse reaction is presupposed to be unimportant. Assuming for the present discussion that $[\ H_2\ ]$ is constant and $p > 0$, and subject to the initial condition $[M_2SO_4] = [M_2SO_4]_o$ at $t = 0$, Equation 8 can be integrated to

$$\frac{[M_2SO_4]_0^{1-p} - [M_2SO_4]^{1-p}}{1-p} = K' [H_2]^m t, \qquad (9)$$

for $p > 0$, $P \neq 1$

Defining the degree of completion of the reaction, x, as

$$x = 1 - \frac{[M_2SO_4]}{[M_2SO_4]_0} \qquad (10)$$

Equation (9) may be written

$$(1-x)^{1-p} = 1 - \frac{K'[H_2]^m (1-p)\, t}{[M_2SO_4]_0^{1-p}} \qquad (11)$$

Curves showing the dependence of the degree of completion, x, on reaction time, t, given by this equation for the the case where $0 < p < 1$ and for the case where $p \geq 1^*$ have positive slopes ($dx/dt > 0$) and negative second derivatives ($d^2x/dt^2 < 0$). When $0 < p < 1$, the curves pass through $x = 1$ at some finite time, indicating the reaction goes to completion in a finite period of time. When $p \geq 1$, on the other hand, the reaction approaches completion asymptotically.

Data from the first twenty-six reduction tests (Appendix, Table A-II) were used to determine the reaction order with respect to sulfate concentration. In these tests the hydrogen pressure (and hence the equilibrium hydrogen concentration) was constant at one atmosphere, and the initial sulfide concentration was zero.

---

*Using the defining relation $\lim_{h \to 0} (1 + h)^{1/h} = e$, one may show that as $p \to 1+$ the solution to Equation 8 is $x = 1 - \exp(-K'[H_2]^m t)$, a limiting form of Equation 11.

Plots of the experimental data, as x against t, for $[M_2S] = 0$ at $t = 0$, are shown in Figure 24. All curves had positive slopes, i.e., $dx/dt > 0$, but an unexpected positive second derivative, $d^2x/dt^2 > 0$, as shown in Figure 2 . The shape of the curves, similar to a plot of $x \propto t^{\alpha}$ with $\alpha > 1$ suggested plotting the x-t data on logarithmic coordinates. The x-t plot on logarithmic coordinates exhibits a family of straight lines, very nearly parallel, as shown in Figure 25.

A first conclusion to be drawn from inspection of the data is that the hydrogen reduction of sulfate is zero order or very nearly so with respect to sulfate concentration; i.e., $p = 0$. If the sulfate concentration influenced the reaction rate, its disappearance as $x \rightarrow 1$ would cause the reaction rate to decrease such that $dx/dt \rightarrow 0$ as $x \rightarrow 1$. But, as seen in Figure 24 the reaction rate does not decrease, and in fact, increases as $x \rightarrow 1$. Hence the concentration of sulfate must have no influence upon the reaction rate.

A second conclusion is that the sulfate reduction is self-catalyzed or auto-catalyzed, either by the water or metal sulfide product. Since the reaction order is zero with respect to sulfate and the hydrogen concentration was virtually constant (values of the exit hydrogen concentration were of the order of 94 mole percent) the rate of reaction would be constant and x - t curves would be straight lines, were the reaction not self-catalyzed. But the reaction rate does increase with product concentration, and so self-catalysis is evident. Because water vapor is continually removed from the reaction mixture by the flow rate of excess hydrogen, it is improbable that it could accumulate and account for the catalysis. It was therefore concluded that the reaction is self-catalyzed by the sulfide,

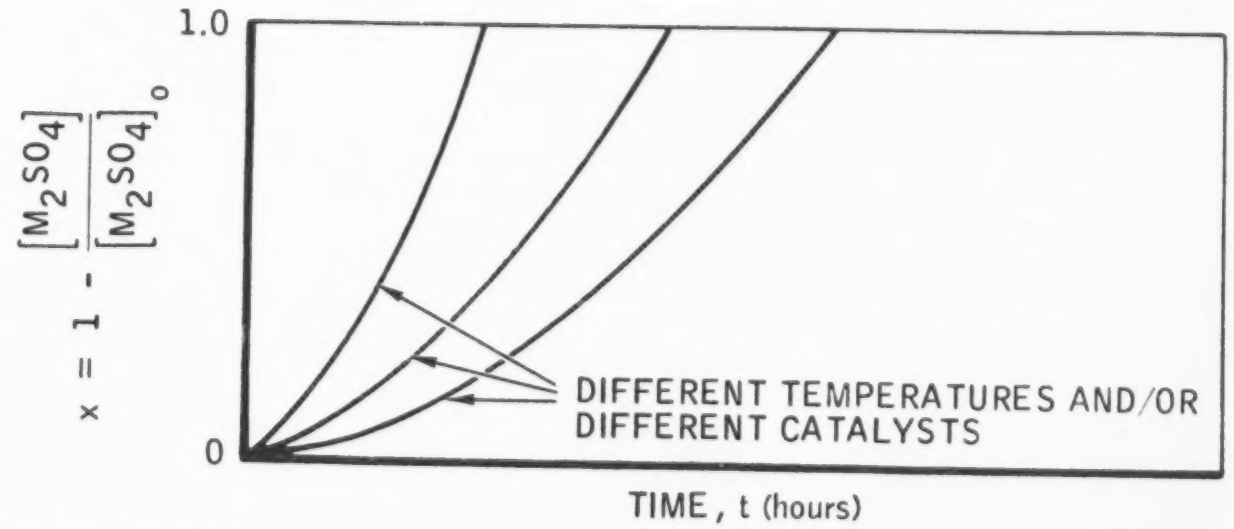

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Figure 24. Typical Plots of the Experimental Data for Hydrogen Reduction of Sulfate Plotted on Linear Coordinates. The Concentration of M_2S is Zero at t = 0.

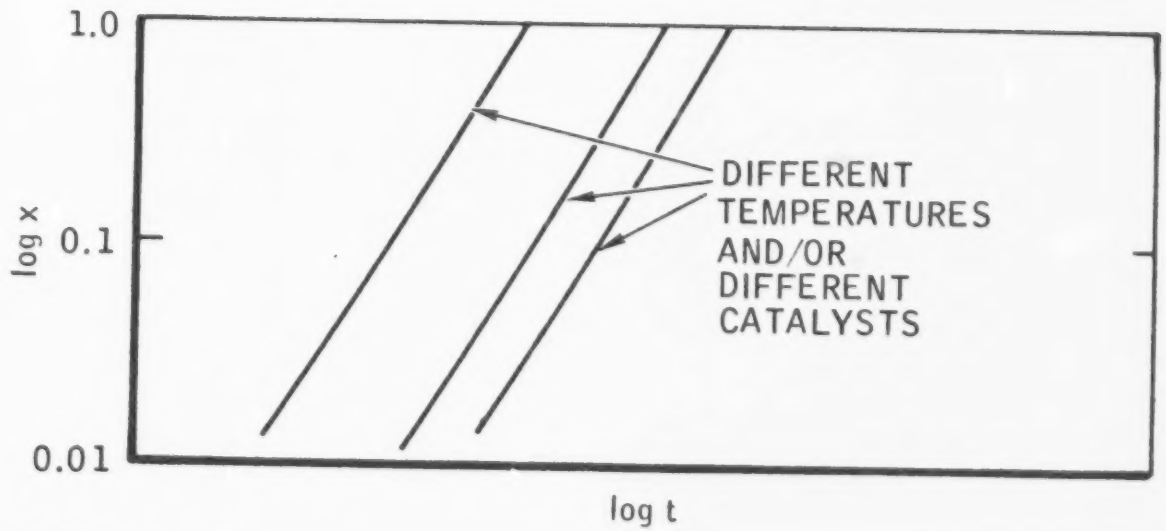

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Figure 25. Form of the x-t Data for Hydrogen Reduction of Sulfate Plotted on Log-Log coordinates. The Concentration of M_2S is Zero at t = 0.

and the data were analyzed to determine the reaction order with respect to sulfide.

B. DETERMINATION OF THE REACTION ORDER WITH RESPECT TO SULFIDE CONCENTRATION

To account for the effect of sulfide, the reaction rate expression is written in the form

$$-\frac{d}{dt}\,[M_2SO_4] = \frac{d}{dt}\,[M_2S] = \left(K\,[H_2]^{m}\right)[M_2S]^{n} \qquad (12)$$

where the overall reaction rate constant K is a function of the kinetic rate constant k, catalyst concentration c, temperature T, and combined mass-transfer effects denoted by A*, that is,

$$K = \text{function}\,(k,T,c,A)$$

Equation 12 may be written as

$$\frac{dx}{dt} = \left(K\,[H_2]^{m}\right)[M_2SO_4]_0^{n-1}\,x^{n} \qquad (13)$$

where

$$x = 1 - \frac{[M_2SO_4]}{[M_2SO_4]_0} = \frac{[M_2S]}{[M_2SO_4]_0} \qquad (14)$$

Subject to the initial condition $x = 0$ at $t = 0$, Equation 13 may be integrated to

$$\frac{x^{1-n}}{1-n} = K\,[H_2]^{m}\,[M_2SO_4]_0^{n-1}\,t \qquad (15)$$

or

$$x = \left\{(1-n)\left(K\,[H_2]^{m}\right)[M_2SO_4]\right\}^{1/1-n}\,t^{1/1-n} \qquad (16)$$

*The combined mass-transfer effects A are dependent upon quantities including the ratio of gas flow rate to reactor volume, bubble size, power delivered to the reactor impeller, and geometry of the impeller and reactor.

The logarithmic plot of $\underline{x}$ vs $\underline{t}$ will yield straight lines (Figure 26 with slopes of 1/(1-n). Denoting the intercept at t = 1 by $x_{t=1}$, ' the value of the product of the reaction rate constant and hydrogen concentration, $K\,[H_2]^m$, is calculated from $K\,[H_2]^m = [x_{t=1}]^{1-n}\,[M_2SO_4]_0^{1-n} / (1-n)\,[H_2]^m$

Data for the reduction reaction when $[M_2S]_0 \neq 0$ cannot be analyzed by the graphical method just described because the solution to Equation 13, $x^{1-n} = x_0^{1-n} + (1-n)\,K\,[H_2]^m\,[M_2SO_4]_0^{n-1}\,t$, does not plot as a straight line on log x-log t coordinates. When $[M_2S]_0 \neq 0$ it is necessary to differentiate the non-linear plot of experimental data x-t numerically, for substitution of dx/dt into Equation 13. This gives

$$\log (dx/dt) = \log \left\{K\,[H_2]^m\,[M_2SO_4]_0^{n-1}\right\} + n \log x \qquad (17)$$

and

$$x = [M_2S] / \left([M_2SO_4]_0 + [M_2S]_0\right) \qquad (18)$$

However, this procedure is not very accurate since "in general, approximate (numerical) differentiation is inaccurate. Its accuracy may be very seriously impaired by small inaccuracies in the tabulated data" (25).

The results of graphical analysis of the data (Appendix Table A-II) are listed in Table XXV. A graph showing several x-t plots on logarithmic coordinates is shown in Figure 26. The mean reaction order with respect to sulfide concentration in the hydrogen reduction of sulfate is calculated from the data to be n = 0.371. The 95% confidence interval of the mean is $0.300 < n < 0.444$ or 0.371 ± 0.071.

C. DETERMINATION OF THE REACTION ORDER WITH RESPECT TO HYDROGEN PRESSURE

The order of the reaction, $\underline{m}$, with respect to hydrogen pressure

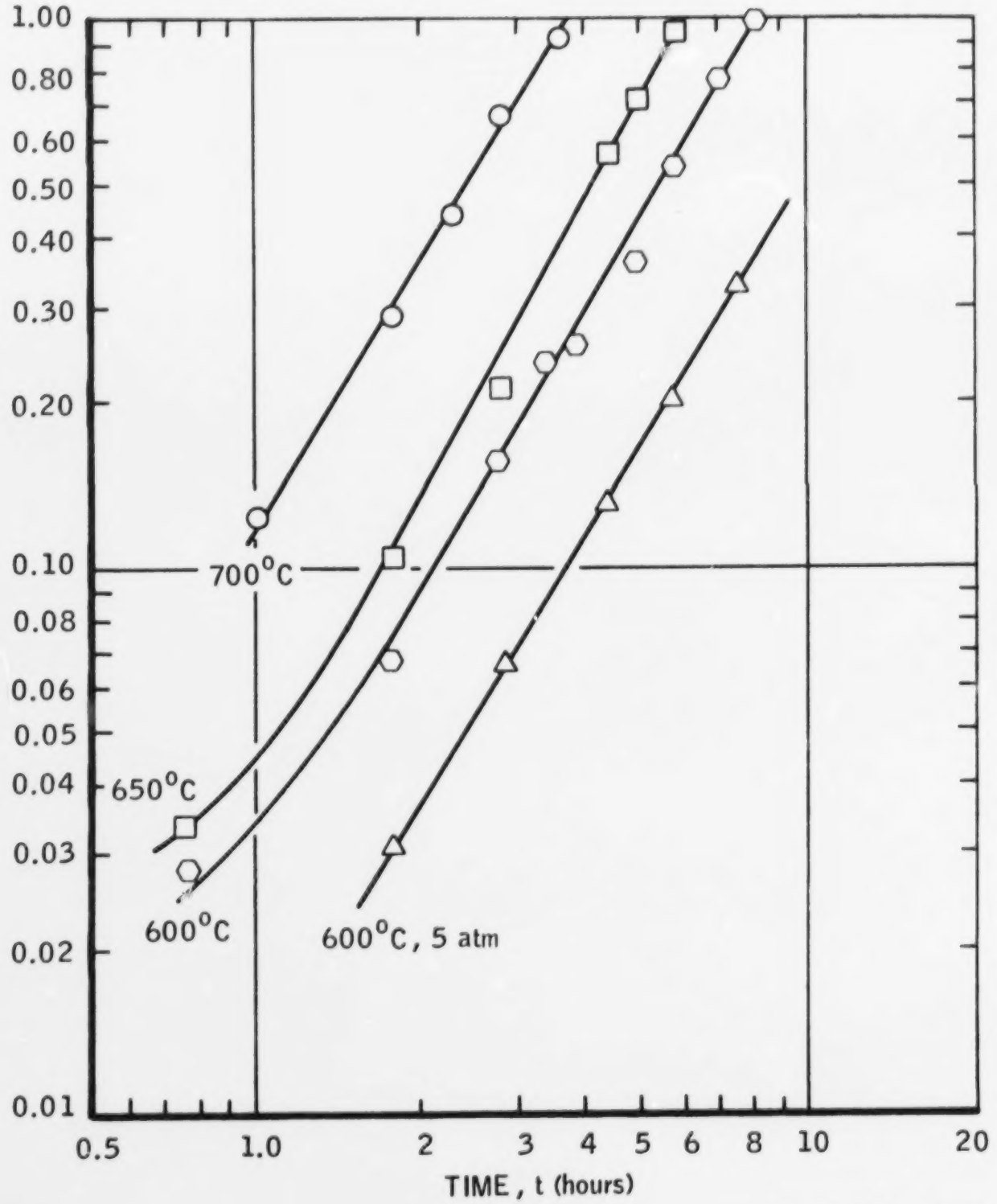

Figure 26. Reduction with H_2. x-t Data Plotted on Logarithmic Coordinates.

Table XXV

Graphical Analysis of the Reduction Data

Run R-G	Temp °C	Catalyst	$[M_2SO_4]$ Mole %	Q/V $\frac{cm^2/sec}{cm^3}$	C mole % catalyst	Fit of line to data	intercept (t=1)	1/1-n	Rxn order n	Rate constant $K^\circ[H_2]^{1/n}$	Region of validity
2	600	none	0.197	0.137	0	exc	0.0031	1.525	0.338	0.0119	0.05<X
3	600	$FeSO_4$	0.188	0.137	4.4	exc	0.0255	1.74	0.425	0.0806	0.05<X
4	600	Fe	0.197	0.137	4.4	exc	0.0096	1.92	0.480	0.0728	0.06<X
5	600	FeS	0.197	0.137	4.4	good	0.0272	1.77	0.435	0.0922	0.06<X
6	700	none	0.197	0.137	0	good	0.032	1.58	0.368	0.0042	0.1<X
9	600	$MnSO_4$	0.188	0.137	4.4	fair	0.0105	1.02	0.020	0.0023	.03<X<.15
12	650	FeSO	0.188	0.137	4.4	exc	0.026	2.14	0.533	0.179	.07<X
13	500	$SnSO_4$	0.188	0.137	4.4	good	0.0086	1.68	0.405	0.0368	.05<X
14	700	$FeSO_4$	0.188	0.137	4.4	good	0.12	1.66	0.398	0.169	0.1<X
16	600	$VOSO_4$	0.188	0.137	4.4	good	0.0026	1.50	0.333	0.0093	.04<X<.40
17	600	$FeSO_4$ (5 atm)	0.188	0.027	4.4	good	0.012	1.68	0.405	0.0449	.03<X<.40
18	650	$FeSO_4$	0.188	0.284	4.4	fair	0.068	1.67	0.401	0.123	0.1<X
19	650	$FeSO_4$ (steam)	0.188	0.137	4.4	poor	0.0095	2.09	0.522	0.102	0.1<X
21	650	$FeSO_4$	0.188	0.137	8.8	exc	0.070	1.83	0.453	0.171	0.1<X
24	650	$FeSO_4$	0.197	0.137	2.5	good	0.0205	1.11	0.10	0.341	0.1<X
25	600	$FeSO_4$	0.197	0.710	4.4	exc	0.325	1.48	0.325	0.231	.04<X<.9

Mean n = 0.371 $\pm$ 0.062 at 95% confidence

can be obtained from the equation

$$\log \left(- \frac{d}{dt} [M_2SO_4] \right) = n \log [H_2] + \log K + n \log [M_2S] \qquad (19)$$

which was derived by taking the logarithm of the basic rate expression (Equation 8). The slope of a plot of log (rate) vs log (hydrogen pressure) will be the desired reaction order. Results of experiments done at six different pressures utilizing otherwise identical conditions are presented in Table XXVI. The logarithms of the results, given in the same table, are plotted in Figure 27.

Table XXVI

The Effect of Hydrogen Pressure on Reduction Rate

H_2 Pressure (atm.)	Log (pressure)	Rate (%/hr between 40-60% completion)	Log (rate)
10	1.00	66.7	1.824
5	0.70	40.8	1.611
2	0.30	27.8	1.444
1	0.00	16.0	1.204
0.5	-0.30	10.3	1.013
0.25	-0.60	(5.8)	0.763
0.215(*)	-0.67	(5.8)	0.763

*Corrected for reaction loss

( ) Estimate

The least squares slope of the curve is 0.646 with a standard deviation of log (rate) about the mean (i.e. 0.646 log (H_2) + 1.190) of 0.041. Using this value it was determined with 90% confidence that the true reaction order is between 0.588 and 0.704. A value of 0.65 will be used.

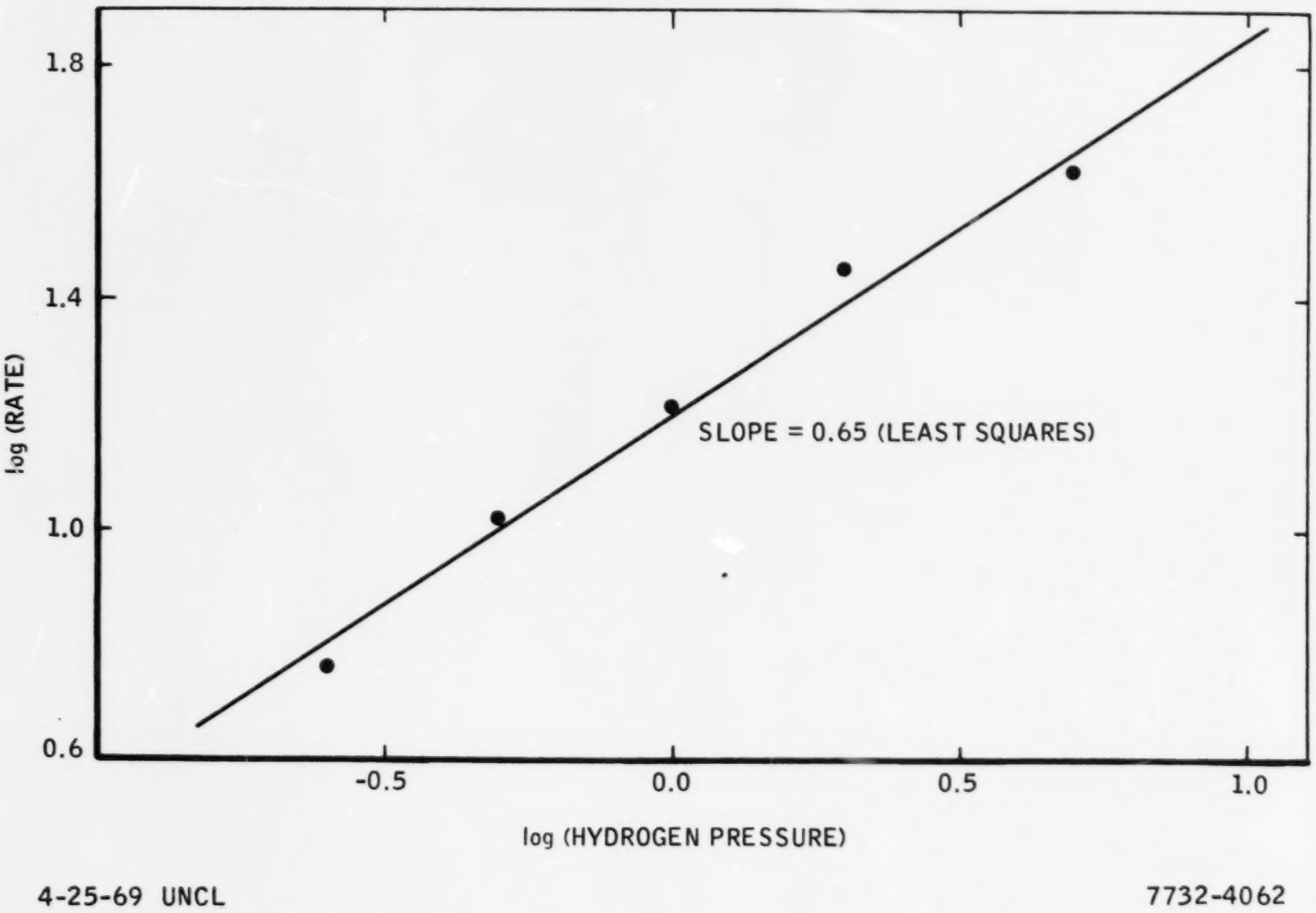

Figure 27. Log (rate of Reduction Between 40 and 60% Completion Based Upon Sulfate) vs. Log (Hydrogen Pressure)

D. EFFECT OF IRON CONCENTRATION

The basic rate expression (Equation 12) is modified in the following manner to account for iron catalysis:

$$-\frac{d}{dt}[M_2SO_4] = K[M_2S]^n[H_2]^m[C + (Fe)^a] \qquad (20)$$

The last term in brackets implies that the reaction proceeds without any iron present (i.e. Fe ≤ 0.1%) and that when iron is present it proceeds at the uncatalyzed rate plus an additional amount which is a function of $(Fe)^a$. Subtracting out the rate when no iron is present, the following expression is applicable:

$$-\frac{d}{dt}[M_2SO_4]_T - \frac{d}{dt}[M_2SO_4]_0 = K[M_2S]^n[H_2]^m[Fe]^a \qquad (21)$$

Here, the first term represents the total actual observed rate and the second term represents the rate when no iron is present. The slope of a logarithmic plot of the actual rate minus the rate with iron content equal to zero versus iron concentration will be the reaction order. The results of several iron-concentration tests are presented in Table XXVII and are plotted in Figure 28.

Table XXVII

Reaction Rate as a Function of Iron Concentration

Iron (%Fe)	Log (Fe)	Reaction Rate (total) (%/hr)	Log (Total rate -rate no Fe)
4.8	0.68	30.3	1.344
2.4	0.38	24.8	1.220
1.3	0.11	23.6	1.188
0.25	-0.60	13.8	0.748
0.094	-1.03	8.1	—
0.009	-2.05	8.2	—

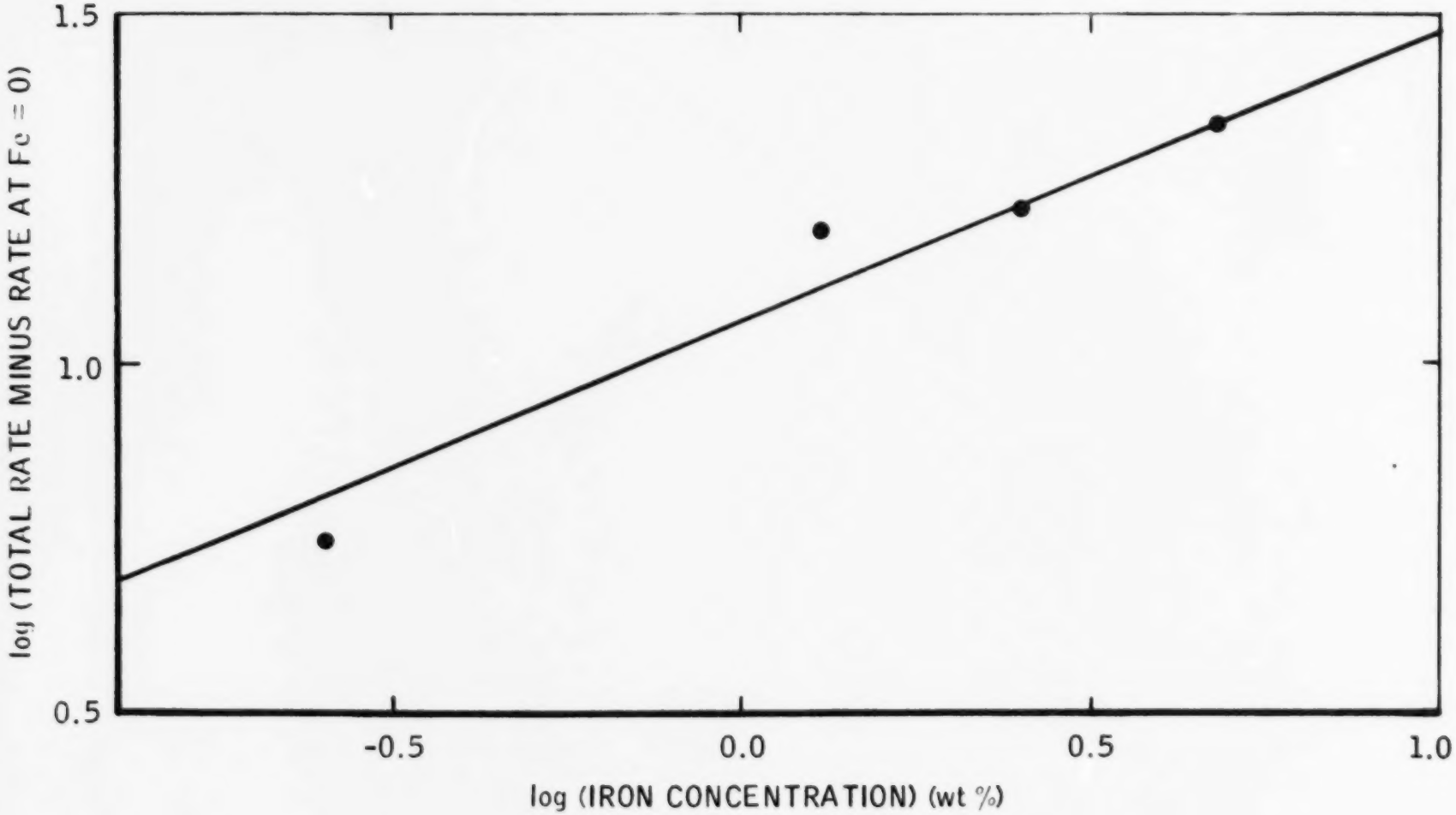

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Figure 28. Log (Additional Rate of Reaction as Caused by Iron) vs. Log (iron concentration) for the Determination of Reaction Order

The least squares slope (i.e. the reaction order) for the curve is 0.41. This number may be somewhat misleading since it suggests that the rate increases quite appreciably with iron concentration. The reason for this is that the reaction rate without iron is a considerable fraction of the rates with iron. Figure 29 is a logarithmic plot of total reaction rate vs iron concentration which gives a slope of 0.31. This pseudo reaction-order more clearly demonstrates the small effect that increasing the iron concentration has on increasing the reduction rate.

The intercept in Figure 29 represents log $(K[M_2S]^n [H_2]^m)$ and is equal to 1.065, or $K [M_2S]^m$ equals 11.6. Using the data at 4.8% iron, C is equal to 0.7 when the rate is given as percent reduction per hour between 25 and 75% completion. The resulting overall equation for describing the reduction rate for sulfate with hydrogen is:

$$\frac{d}{dt}[M_2SO_4] = K [M_2S]^{0.37} [M_2SO_4]^{0.0}{}_x [H_2]^{0.65} [0.7 + (Fe)^{0.41}] \quad (22)$$

E. TEMPERATURE EFFECT

Temperature effects in a rate expression of the form

$$\frac{d[A]}{dt} = K [A]^{\alpha} [B]^{B} \ . \ . \ . \quad (23)$$

are contained in the rate constant K. The order of the reaction, if the expression correctly represents the reaction kinetics at all temperatures under consideration, is independent of temperature. As a check on the basic rate expression (Equation 13)

$$\frac{dx}{dt} = (K [H_2]^m) [M_2SO_4]_0^{n-1} x^n \ , \quad (24)$$

the invariance of the reaction order with temperature was tested with the data of Table XXV.

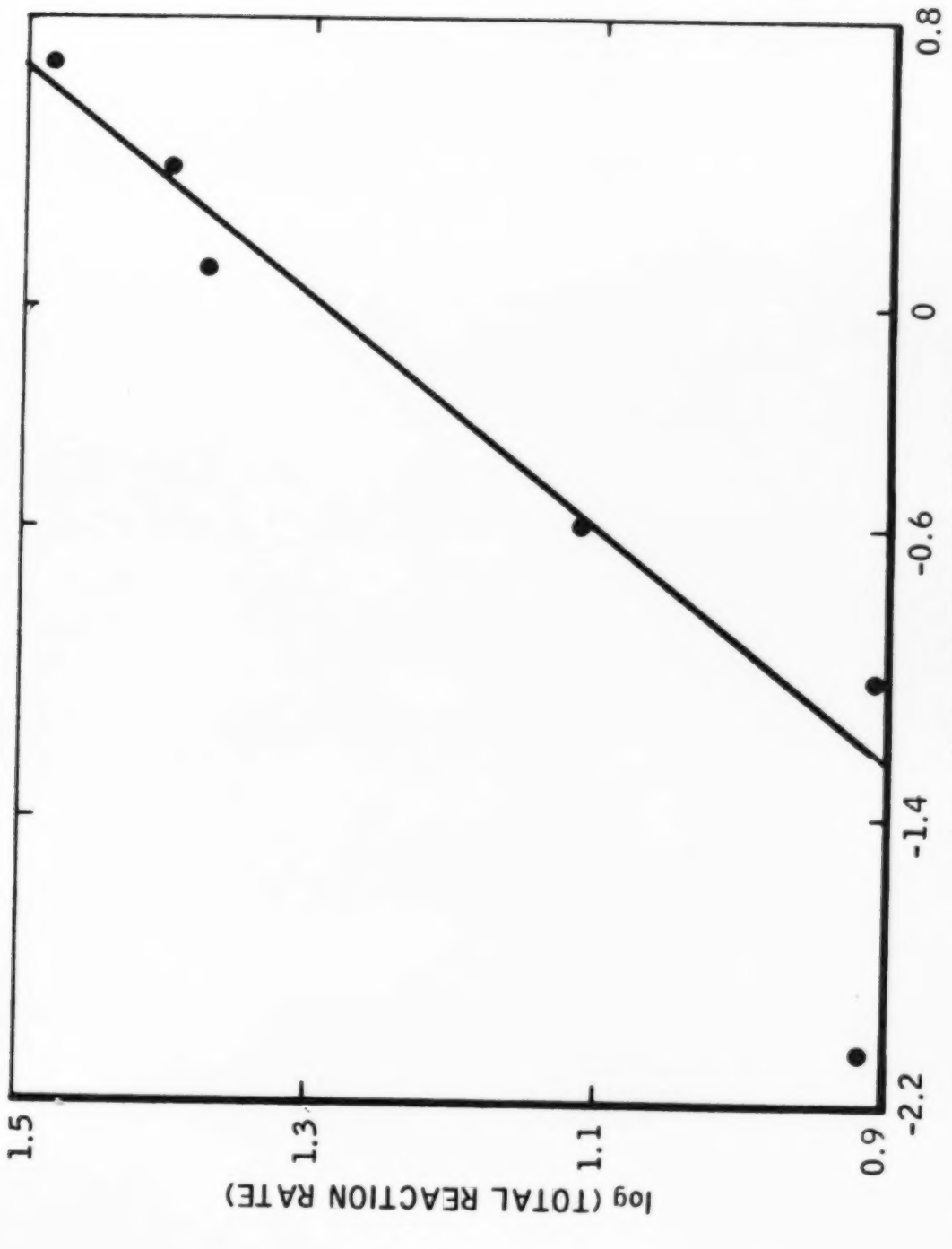

Figure 29. Log-Log Plot of Total Reaction Rate vs. Iron Concentration for the Reduction of Sulfate with Hydrogen at 650°C

Using all of the observations at T = 600, 650, and 700°C (the datum for 500°C, being a single observation, could not be included) in Table XXV, the hypotheses that $\bar{n}_{600°} = \bar{n}_{700°}$ was tested in a completely randomized analysis of varience or F test (32). Here, $\bar{n}$ denotes the mean value of the observations at a given temperature. The computed value of the statistic F = 2.27 with 2 and 12 degrees of freedom at the 5 percent level of significance leads to acceptance of the hypotheses. Accordingly, the data indicate that the reaction order in sulfide, n, is independent of temperature.

All effects of temperature in the overall reaction rate constant K should be contained in the kinetic rate constant k; that is, K(T, other variables) = K(k(T), other variables). While K is dependent upon several other variables including the gas-flow-rate to liquid-volume ratio G/V, catalyst concentration c, catalyst species, and reactor geometry, it is assumed that these effects are separable, i.e.,

$$K = k(T) f\,(G/V)\; f\,(c)\; \pi_i f_i \tag{25}$$

where f denotes "a function of" and $\pi_i f_i$ the product of all other functions of variables influencing K.

Equation 25 may be rearranged to

$$k = \frac{K}{f\,(G/V) f\,(c)\; \pi_i f_i} \tag{26}$$

The Arrhenius relation

$$\frac{d \ln k}{dT} = \frac{\Delta E^*}{RT^2} \tag{27}$$

where ΔE^* is energy of activation, combined with Equation 26, can be integrated to

$$\ln K_2 - \ln K_1 = \frac{\Delta E^*}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \tag{28}$$

The functions, f(G/V), f(c), $\pi_i f_i$ being constant among experiments, drop out of Equation 28. The only runs listed in Table XXV from which ΔE^* can be inferred with confidence are Experiments 2 and 6 and Experiments 3, 12 and 14. In these two sets of runs the experimental conditions (G/V, c, etc.) are constant among runs within a set. A plot of log K versus 1/T yields a value of $\Delta E^* = 28.0 \pm 0.05$ kcal/ g mole for the iron-catalyzed reduction.

The final overall rate expression for reduction with hydrogen is given by equation 22. This expression can be used in designing the hydrogen reducer for the Molten Carbonate Process, in a manner similar to that outlined by Kingsly and Bliss (28). If carbon (coke) is used as the reducing agent, a new relationship will have to be derived, expressing the overall carbon reduction rate. The few tests done with coke are not sufficient for this; more coke reductions are needed. It is planned to study the coke reduction process thoroughly in the next report period, because there are potential economic advantages to using coke as the reducing agent.

V. MECHANISTIC INTERPRETATION

A. THE ROLE OF SULFIDE AND SULFATE

Mechanistic information concerning any reaction may be deduced from the kinetic expression, intermediate identification, or a combination thereof. There are definite indications that intermediates are formed in the sulfate reduction reaction, although none have yet been identified. The fact that the reaction is zero order or very nearly zero order with respect to sulfate demonstrates that sulfate itself is not involved in the rate determining step of the mechanism and suggests that some other sulfur-containing compound is actually being reduced. In addition, the color of the melt during the reduction is maroon (when solidified is orange) while at the outset and the conclusion the melt is normally colorless. This color must be attributed to a sulfur-containing intermediate since neither the reactant, sulfate; the product, sulfide; nor the solvent, carbonate, has any appreciable color.

It is not known for sure that the colored intermediate is the reactive one, but the coloration is always more pronounced during the rapid phases of the reduction.

Identification of the intermediate via absorption spectra has not been undertaken. However, the kinetic expression and certain knowledge of sulfur chemistry allows one to suggest possible intermediates and routes forming those intermediates.

Since the reaction is autocatalytic with respect to sulfide, and since sodium sulfate has not been observed to undergo appreciable simple self-decomposition at these temperatures, it is likely that sulfide and sulfate react to form the intermediate. Further indication of this rests in the fact that the simple combination of sulfate and sulfide in molten carbonate has been found sufficient for the formation of the colored species. Some possible reactions and intermediates are as follows:

$$3M_2SO_4 + M_2S \longrightarrow 4M_2SO_3 \quad (28)$$

$$M_2SO_4 + M_2S \longrightarrow M_2S_2O_3 + M_2O \quad (29)$$

$$M_2SO_4 + 7M_2S \longrightarrow 4M_2S_2 + 4M_2O \quad (30)$$

$$2M_2SO_4 + 2M_2S \longrightarrow M_2S_2 + 2M_2SO_3 + M_2O \quad (31)$$

One requirement for the sulfur-containing intermediate is that it must be somewhat stable in order for it to exist in a concentration sufficient for reaction. Thus, the intermediates of sulfite. thiosulfate, and polysulfide are reasonable choices.

The first of the above reactions is not likely since, first of all, sulfite does not have a characteristic maroon color and, secondly, in the presence of iron oxide, sulfite is extremely unstable at temperatures above 600°C. Furthermore, sulfite was not only found to be more unstable in the presence of ferric oxide, but the reduction of sulfite was not enhanced by iron. Reaction 29 is somewhat more likely than Reaction 28 because when thiosulfate is dissolved in carbonate, the maroon color is noted. However, thiosulfate is not very stable and the coloration may be a result of the

formation of the decomposition products. The intermediate that appears most likely at this time is polysulfide because of its stability up to temperatures of 1300°C(1) and because the color of a polysulfide melt containing traces of iron is nearly identical to that of the melt during reduction. In addition, formation of polysulfide via Reaction 30 involves only one sulfate for seven sulfides explaining how the reaction order with respect to sulfate could be nearly zero. Furthermore, the addition of iron, forming the very stable pyrite (FeS_2), would conceivably increase the reaction rate. Also, the reaction between iron and sulfur (a mechanism of which is discussed below) is quite well known. Thus, the reaction which satisfies all experimental results to date involves the reduction of sulfate with sulfide to form polysulfide. Further support for this step is realized by noting similar well-known reactions; for example, the reduction of concentrated sulfuric acid by hydrogen sulfide:

$$H_2SO_4 + H_2S \longrightarrow S + 2H_2O + SO_2 \qquad (32)$$

or the reduction of sulfur dioxide by hydrogen sulfide:

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O \qquad (33)$$

B. THE ROLE OF IRON

There are at least three distinct ways in which iron could catalyze the reduction:

(1) Act as a heterogeneous (surface) catalyst.

(2) Form more stable sulfur-containing intermediates.

(3) Act directly in reducing the sulfate or the reactive intermediate.

The first of these is unlikely since sulfide, usually a very severe poison for surface-catalysis, acts to further increase instead of decrease the reaction rate. In addition, all iron compounds, including metallic iron, are equally

effective. Since heterogeneous catalysis is critically dependent on surface, this strongly indicates that this phenomena is not occuring.

The second possible role for iron, i.e., the formation of a stable* reactive sulfur-containing intermediate, would produce a faster reaction due to the fact that higher concentrations of the intermediate species would exist. A corollary to this would be that the role of iron may be one of producing an unstable reactant; for example, the stability of ferrous sulfate (a possible reactant formed as a result of adding iron compounds to the melt) is much less than the alkali sulfate. An instability of the reactant may cause a concentration increase of the intermediate since the relative stability of the intermediate is greater with respect to the more unstable reactant. Thus, ferrous sulfate may decompose forming the reactive intermediate more readily (and thus causing a greater concentration of the intermediate) than the alkali sulfate. This sort of interaction between iron and the intermediate or the reactant has not yet been investigated and, as a result, nothing definite can be stated at this time.

The last of the three roles for iron involves a mechanism whereby iron itself reduces the sulfate or sulfur-containing intermediate, forming iron oxide, and reduction of the iron oxide with hydrogen back to metallic iron or a lower oxide. For such a reaction to be feasible, the free energy of the two reactions

$$8Fe + 3M_2SO_4 \longrightarrow 4Fe_2O_3 + 3M_2S \qquad (34)$$

$$Fe_2O_3 + 3H_2 \longrightarrow 3H_2O + 2Fe \qquad (35)$$

*Stability refers to the stability of the compound as compared to its decomposition products not as compared to the reducing agent. For example, sulfite is unstable in the presence of iron forming sulfide and sulfate, but at the same time its stability with reference to the reducing agent, hydrogen, is unchanged in the presence of iron. Thus, iron makes sulfite unstable.

must be favorable. Thermodynamic calculations show this to be the case with several other metals (e.g., Mo, Ge, & Sn) as well as iron. It is interesting to note that of all the other metals tried as catalysts, only tin (in addition to iron) was significantly effective. This sort of indirect information supports the theory that iron is directly involved in the reduction. However, further intermediate identification is necessary before a conclusive mechanistic scheme can be derived.

C. THE ROLE OF HYDROGEN

The role of hydrogen in the reduction mechanism can involve one of several steps and as a result is quite difficult to ascertain. Hydrogen can react at the surface as hydrogen atoms or hydrogen molecules, it can react as a soluble species in the melt, it can react heterogeneously on a third body or it can reduce some species that in turn reduces the sulfate. The only available knowledge concerning hydrogen's role is that as the pressure is increased, the rate of reaction is similarly increased. Sufficient information is not available to deduce the mechanism which involves hydrogen; although it should be mentioned at this point that a gas phase reaction between hydrogen and some gaseous sulfur containing species appears unlikely. This is suggested by the fact that most sulfur containing species (e.g., CS_2, SO_2, SO_3, and H_2S) are readily absorbed in the melt and, also, a pyrolysis experiment (Experiment 52) produced no measurable sulfur-containing species in the gas phase up to temperatures of 940°C.

VI. RECOMMENDED CONDITIONS AND REDUCING AGENTS

A. BELOW 650°C

Below 650°C the data conclusively demonstrate that hydrogen is the most active reducing agent. This conclusion is in accord with what other

workers have found. It should be pointed out however, that hydrogen is one of the more expensive reducing agents, so it may be more economical to use a less expensive mixture of hydrogen and carbon monoxide, even though this would result in somewhat slower reduction rates.

In utilizing the process chemistry data for the design of larger hydrogen reduction vessels there are two important points to consider. The first is that the reaction is zero order with respect to sulfate. This means that the rate but not the total reaction time is the same whether there is an ounce or ton of material to reduce, assuming like conditions.

The second consideration is the extent of contact between the gas and liquid phase. Process chemistry data has very little information in this regard. One packed bomb test utilizing very roughly 0.05 lbs M_2SO_4/ft^2 of contact area was found to go about 3.1 times faster (in %/hr) than a test utilizing a bubble-type contactor employing 2.5 times as much initial sulfate. Taking into consideration the amount of material present, the rates in moles or lbs per hour for the two tests were only about 25% different. Since nearly all the experiments were carried out in bubble-type contactors, the rates (%/hr) should probably be multiplied by 3.1 to get the expected rate in a packed bomb where an approximate surface area has been estimated. This number is then multiplied by 0.0005 lbs M_2SO_4/ft^2 to obtain the rate in lbs of sulfate reduced per hour per square foot. The result is a number independent of concentration but probably dependent on surface area.

To determine the effect of time (or alternatively the distance hydrogen has traveled through a flow contactor) the following rate expression was employed:

$$-\frac{dH_2}{dt} = K(H_2)^{0.65} \qquad (36)$$

The assumption was made that catalyst (i.e. sulfide and iron) concentrations were constant throughout the contactor; in addition, the boundary condition was that at t = 0, (H_2) = 10 atm. Using this information Figure 30 was prepared. The average hydrogen pressure (assuming 85% utilization of the reducing gas) was calculated to be 4.9 atm. Therefore the average rate will be a function of 0.49 times the initial hydrogen pressure. This information was utilized in calculations for determining rates as a function of different conditions, given in Table XXVIII.

Table XXVIII

HYDROGEN REDUCTION RATES

	Reduction Rate (%/hr)(1)			
		Iron and Sulfide (2.4 and 10 wt%, respectively)		
Temp (°C)	Control(2)	1 atm.(3)	5 atm.(3)	10 atm.(3)
500	1.6	15	44	88
600	6.5	30	87	176
700	26	60	174	352
800	104	120	348	704

(1) 1%/hr equals about 0.0005 lbs/sq. ft/hr.

(2) Initial pressure one atmosphere (no catalyst)

(3) Initial pressure (average pressure is 0.49 x initial pressure)

B. ABOVE 650°C

In the temperature range of 650-750°C there appears to be no satisfactory reducing agent. Although hydrogen is still the most active in this range, it would be easier to accomplish faster reductions by changing factors

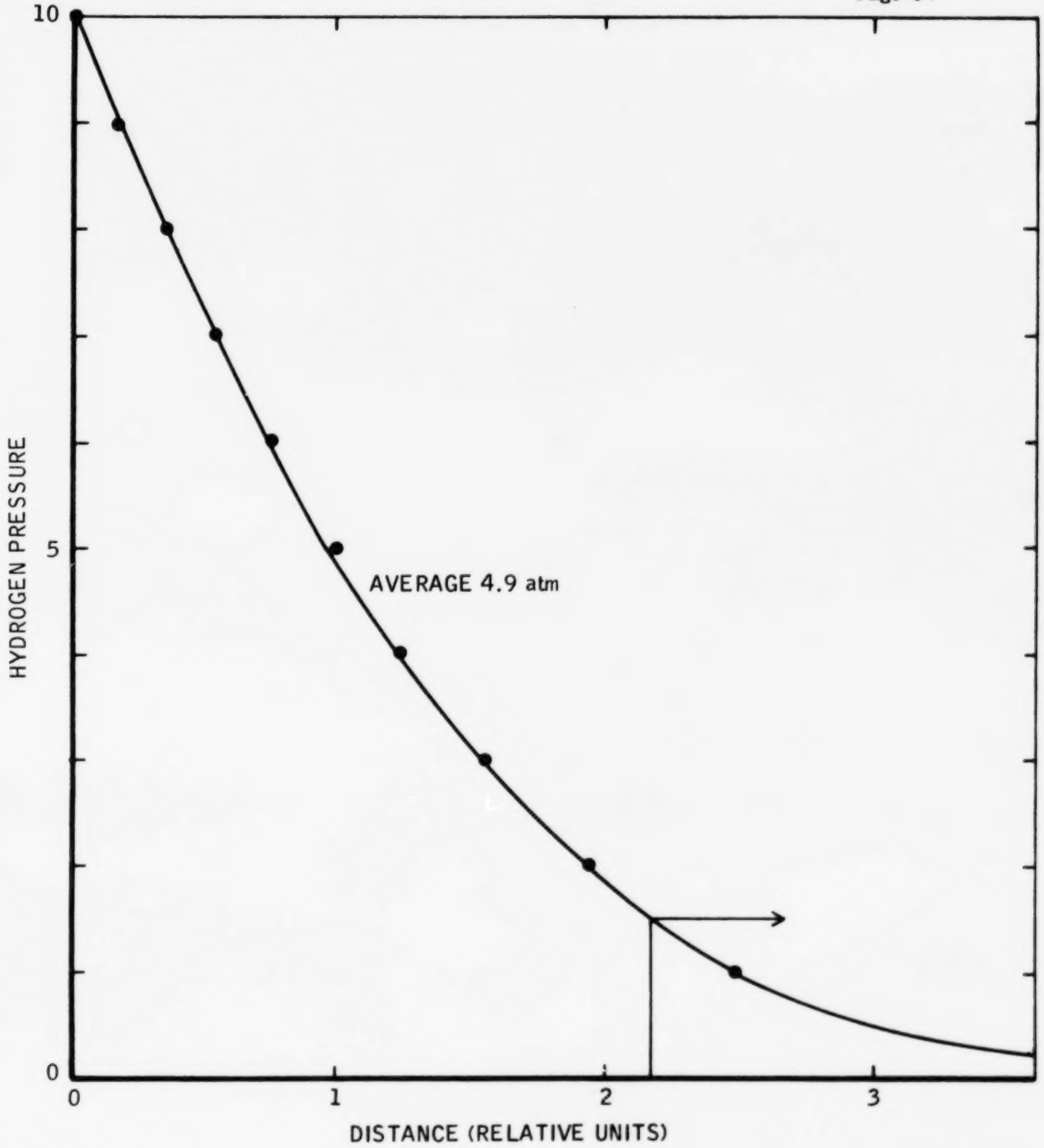

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Figure 30. H_2 Pressure as a Function of Distance Traveled Through a Reactor

other than temperature, e.g. pressure, surface contact, etc. On the other hand, fluidized coke in this temperature range is much too inactive for commercial use.

At 750°C and above, there appears to be no advantage to using hydrogen. Instead, fluidized coke appears better, due to its high reducing activity, low cost, and applicability to internal heating by combustion in limited amounts of air. At 800°C it was found that the rate of reduction was 0.77 lbs M_2SO_4/hour/150 cc utilizing 2.5 times the stoichiometric amount of fluidized coke. However, the chemistry and engineering aspects of the coke reduction process will have to be studied much more thoroughly before coke can be chosen as the preferred reducing agent.

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APPENDIX

TABLE A-I

SALT MAKEUP

Make-up Number	Test	Na_2CO_3 (g) (1)	Na_2S (g)	Na_2SO_4 (g)	K_2CO_3 (g)	Li_2CO_3 (g)	$FeSO_4 \cdot 7H_2O$ (g)	Other Catalysts
1	Control	37.0	0	84.9	100.8	100.8	0	0
2	$FeSO_4$ Catalyst (0.05%)	37.0	0	84.9	100.8	100.8	0.90	0
3	$FeSO_4$ Catalyst (0.23%)	37.0	0	84.9	100.8	100.8	3.70	0
4	$FeSO_4$ Catalyst (1.3%)	45.0	0	74.2	100.8	100.8	20.2	0
5	$FeSO_4$ Catalyst (2.4%)	52.4	0	64.3	100.8	100.8	40.3	0
6	$FeSO_4$ Catalyst (4.8%)	67.2	0	44.4	100.8	100.8	80.6	0
7	$FeSO_4$ Catalyst (9.6%)	97.9	0	3.2	100.8	100.8	161.2	0
8	Other Catalyst ($SO_4^=$ form)	52.4	0	64.3	100.8	100.8	0	0.14 moles
9	Other Catalyst (not $SO_4^=$ form)	37.0	0	84.9	100.8	100.8	0	0.14 moles
10	Sulfide Catalyst (10 wt % initial)	10.8	37.1	84.9	100.8	100.8	0	0
11	Sulfide Catalyst (with iron)	26.2	37.1	64.3	100.8	100.8	40.3	0
12	Packed Bomb	21.0	0	25.7	40.3	40.3	16.1	0
13	Sulfide Catalyst (high concentration with iron)	0.0	74.2	79.0 (2)	38.2	100.8	40.3	0
14	Disproportionation (no iron)	30.6	0	75.0 (3)	100.8	100.8	0	0
15	Disproportionation (with Fe_2O_3)	30.6	0	75.0 (3)	100.8	100.8	0	13.7 g
16	Reduction Fe_2O_3	100.0	0	0	100.0	100.0	0	14.4 g

(1) Referred to in Table A-II

(2) K_2SO_4

(3) Na_2SO_3 (equivalent to 67.0 g M_2SO_4 after disproportionation)

TABLE A-II

EXPERIMENTAL DATA

Experiment No. and Conditions	Time (hr)	Melt Composition (wt %)					Off Gas (g)		Percent Reduction
		M_2CO_3	M_2SO_3	M_2S	M_2SO_4	Fe	CO_2	H_2O	
1. 2.9 ℓ/min H_2, 600°C, 1 atm, no sulfide, no catalyst, SS graphite packed bomb	0	79.5	0	0	25.4	-	-	0	0
	0.417	77.4	0	0.25	24.9	0.02	-	-	2.0
	1.167	79.2	0	1.59	23.3	0.09	-	2.5	8.3
	1.667	80.8	0	3.08	20.5	0.21	-	5.5	19.3
	2.417	80.3	0	7.4	12.6	0.82	-	12.5	50.4
	3.167	86.6	0	13.8	0.82	1.74	-	20.2	96.8
2. 1.4 ℓ/min H_2, 600°C, 1 atm, no sulfide, no catalyst, bubbler contactor, Make-up-1 (refer to Table A-I)	0.00	75.2	0	0	25.4	-	-	0	0
	1.50	74.6	0	0.3	25.0	-	0.6	1.6	1.6
	3.50	76.2	0	0.5	24.7	-	-	1.4	2.8
	6.50	75.6	0	1.4	24.0	-	-	2.8	5.5
	10.00	76.8	0	2.0	22.7	-	-	4.7	10.6
	13.50	75.6	0	3.2	21.4	0.0022	-	7.0	15.7
	18.25	76.9	0	5.0	18.8	-	-	10.5	26.0
	22.00	76.9	0	6.4	17.0	-	-	13.9	31.5
	26.00	76.3	0	9.2	13.5	-	-	18.2	46.9
	31.00	76.3	0	11.5	9.5	-	-	23.5	62.6
	36.00	77.8	0	15.8	5.4	-	-	28.5	78.7
	42.50	76.9	0	17.3	1.7	-	-	32.8	93.3
3. 1.4 ℓ/min H_2, 600°C, 1 atm, no sulfide, 2.4% Fe ($FeSO_4$), Make-up-5	0.00	74.5	0	0.1	25.0	-	-	0	0
	0.75	76.0	0	0.6	24.3	-	-	1.1	2.8
	1.75	71.7	0	0.9	23.3	-	-	2.7	6.8
	2.75	67.0	0	1.9	21.1	-	-	5.1	15.6
	3.75	70.2	0	3.5	18.6	-	-	8.8	25.6
	4.75	67.3	0	5.6	15.9	-	-	13.9	36.4
	5.75	76.2	0	9.2	11.3	-	-	16.9(1)	54.8
	6.75	78.5	0	15.8	5.2	-	-	24.4	79.2
	8.00	73.5	0	17.5	0.1	-	-	32.7	99.6
4. 1.4 ℓ/min H_2, 600°C, 1 atm, no sulfide, 2.4% Fe (metallic), Make-up-9	0.00	77.1	0	0	26.3	-	-	0	0
	0.75	78.9	0	0.2	25.9	-	-	0.4	1.5
	1.75	76.5	0	0.6	25.0	-	-	1.2	4.9
	3.75	75.5	0	1.2	23.0	-	-	2.7	12.5
	5.75	74.0	0	4.1	19.2	-	-	7.8	27.0
	7.75	75.2	0	8.0	13.2	-	-	15.7	49.8
	9.95	77.7	0	13.4	5.8	-	-	22.7	77.6
	11.00	80.5	0	17.3	0.4	-	-	28.5	98.5
	12.00	78.6	0	18.2	0	-	-	30.0	100
5. 1.4 ℓ/min H_2, 600°C, 1 atm, no sulfide, 2.4% Fe (FeS), Make-up-9	0.00	70.7	0	2.0	27.0	-	-	0	0
	0.75	72.8	0	2.1	26.8	-	-	1.1	0.7
	1.75	71.2	0	3.3	25.0	-	-	3.2	7.4
	2.75	68.6	0	6.0	22.5	-	-	6.2	16.7
	3.75	70.0	0	8.4	18.8	-	-	10.0	30.4
	4.75	71.3	0	11.6	13.9	-	-	15.0	48.5
	5.75	75.7	0	16.1	8.1	-	-	20.4	70.0
	6.75	77.7	0	21.4	1.6	-	-	25.7	94.1
	8.00	77.2	0	23.4	0	-	-	28.3	100

TABLE A-II (Continued)

Experiment No. and Conditions	Time (hr)	Melt Composition (wt %)					Off Gas (g)		Percent Reduction
		M_2CO_3	M_2SO_3	M_2S	M_2SO_4	Fe	CO_2	H_2O	
6. 1.4 ℓ/min H_2, 700°C, 1 atm, no sulfide, no catalyst, Make-up-1	0.00	80.0	0	0	26.3	-	-	0	0
	1.00	78.8	0	0.9	24.7	-	-	2.5	6.1
	2.25	76.0	0	2.1	23.1	0.0050	-	5.9	12.2
	3.75	76.8	0	4.8	19.4	-	-	11.1	26.2
	5.25	78.0	0	7.7	14.6	-	-	17.6	44.5
	6.75	79.0	0	12.4	8.9	-	-	25.2	66.2
7. 1.4 ℓ/min H_2, 600°C, 1 atm, no sulfide, 0.14 moles $CuSO_4$, Make-up-8	0.00	78.0	0	0	25.8	-	-	0	0
	2.50	80.5	0	0	-	-	-	1.3	-
	5.00	80.1	0	0	-	-	-	2.3	-
	8.00	76.5	0	0.4	-	-	--	3.5	-
	12.00	77.7	0	1.2	24.5	-	-	5.2	5.0
8. 1.4 ℓ/min H_2, 600°C, 1 atm, no sulfide, 0.14 moles Cr_2O_3, Make-up-9	0.00	76.4	0	0	26.0	-	-	0	0
	3.00	74.2	0	0.4	-	-	-	1.4	-
	6.00	73.2	0	1.0	-	-	-	3.0	-
	12.00	72.1	0	2.7	22.2	-	-	7.1	14.6
9. 1.4 ℓ/min H_2, 600°C, 1 atm, no sulfide, 0.14 moles $MnSO_4$, Make-up-9	0.00	75.3	0	0	26.2	-	-	0	0
	2.50	70.0	0	0.3	25.4	-	-	0.9	3.0
	6.00	73.0	0	1.8	24.5	-	-	2.8	6.5
	12.25	73.8	0	2.1	22.6	-	-	6.6	13.8
10. 1.4 ℓ/min CO, 700°C, 1 atm, no sulfide, no catalyst, Make-up-1	0.00	77.5	0	0	26.8	-	0	-	0
	1.00	78.1	0	0.1	26.2	-	2.0	-	2.2
	3.75	81.5	0	0.7	25.3	0.0018	8.3	-	5.6
	6.75	77.5	0	1.4	24.3	-	12.5(1)	-	9.3
	11.75	81.5	0	3.9	20.8	-	-	-	25.4
	21.50	86.5	0	20.0	0	0.0085	-	-	100.0
11. 1.4 ℓ/min H_2, 600°C, 1 atm, no sulfide, 0.14 moles $NiSO_4$, Make-up-8	0.00	75.3	0	0	24.8	-	-	0	0
	1.50	75.0	0	0	-	-	-	1.0	-
	3.50	76.8	0	0	-	-	-	2.4	-
	5.50	76.8	0	0.7	24.6	-	-	3.8	0.8
12. 1.4 ℓ/min H_2, 650°C, 1 atm, no sulfide, 2.4 % Fe ($FeSO_4$), Make-up-5	0.00	75.5	0	0.1	26.1	2.47	-	0	0
	0.75	72.4	0	0.6	25.2	-	-	1.4	3.4
	1.75	69.3	0	2.2	23.3	2.06	-	4.6	10.7
	2.75	70.9	0	4.4	20.1	2.29	-	9.1	23.0
	3.50	72.0	0	6.9	16.2	-	-	13.9	37.9
	4.25	73.2	0	9.7	11.3	2.49	-	20.0	56.7
	4.75	73.4	0	13.4	7.2	2.59	-	24.6	72.4
	5.50	77.5	0	17.4	0.9	-	-	32.5	96.6

Experiment No. and Conditions	Time (hr)	Melt Composition (wt %)					Off Gas (g)		Percent Reduction
		M_2CO_3	M_2SO_3	M_2S	M_2SO_4	Fe	CO_2	H_2O	
13. 1.4 ℓ/min H_2, 600°C, 1 atm, no sulfide, 0.14 moles $SnSO_4$, Make-up-8	0.00	73.8	0	0.0	24.2	-	-	0.0	0.0
	3.00	70.2	0	0.1	22.9	-	-	4.1	5.4
	6.00	70.9	0	0.2	19.7	-	-	8.8	18.6
	9.00	74.2	0	5.2	15.9	-	-	14.6	34.3
	15.00	74.2	0	11.6	4.0	-	-	29.2(1)	83.5
14. 1.4 ℓ/min H_2, 700°C, 1 atm, no sulfide, 2.4% Fe ($FeSO_4$), Make-up-5	0.00	74.9	0	0.0	26.2	-	-	0.0	0.0
	1.00	72.4	0	2.1	23.0	-	-	4.1	12.2
	1.75	71.0	0	5.3	18.7	-	-	10.0	28.6
	2.25	72.0	0	9.0	14.7	-	-	13.8(1)	43.9
	2.75	71.1	0	12.8	8.8	-	-	21.0	66.4
	3.50	75.9	0	17.0	2.1	-	-	28.8	92.0
15. 1.4 ℓ/min H_2, 600°C, 1 atm, no sulfide, 0.14 moles Mo, Make-up-9	0.00	74.2	0	0.2	25.1	-	-	0.0	0.0
	3.00	71.3	0	3.2	21.0	-	-	3.1	16.3
	6.00	72.0	0	4.6	18.0	-	-	7.4	28.3
	9.00	71.7	0	6.1	16.0	-	-	10.8	36.3
	13.00	71.0	0	8.8	12.5	-	-	16.1	50.2
	17.25	73.4	0	11.8	8.6	-	-	22.1	65.7
	21.50	72.4	0	14.3	5.0	-	-	26.9	80.1
16. 1.4 ℓ/min H_2, 600°C, 1 atm, no sulfide, 0.14 moles $VOSO_4$, Make-up-9	0.00	69.5	0	0.0	26.2	-	-	0.0	0.0
	3.50	71.5	0	0.1	24.6	-	-	2.4	6.1
	6.50	70.2	0	2.2	22.7	-	-	5.2	13.4
	13.50	67.6	0	6.6	17.2	-	-	13.4	34.4
	20.50	70.9	0	14.0	10.6	-	-	24.5	59.5
	25.75	76.1	0	15.8	5.7	-	-	31.9	78.2
17. 1.4 ℓ/min H_2, 600°C, 5 atm, no sulfide, 2.4% Fe ($FeSO_4$), Make-up-5	0.00	67.8	0	0.0	25.1	-	-	0.0	0.0
	0.75	71.0	0	0.0	25.4	-	-	0.4	0.0
	1.75	65.0	0	0.8	24.6	-	-	1.8	3.1
	2.75	72.2	0	1.9	23.7	-	-	3.5	6.7
	4.25	71.3	0	2.8	22.1	-	-	-	13.0
	5.75	66.3	0	4.7	19.9	-	-	-	21.7
	7.25	74.3	0	6.6	17.0	-	-	-	33.1
18. 2.9 ℓ/min H_2, 650°C, no sulfide, 1 atm, 2.4% Fe($FeSO_4$), Make-up-5	0.00	73.7	0	0.3	26.4	-	-	0.0	0.0
	0.75	69.7	0	1.2	24.8	-	-	1.4	6.1
	1.75	72.1	0	3.4	21.7	-	-	6.6	17.8
	2.50	71.1	0	7.1	16.6	-	-	13.7	37.1
	3.00	70.4	0	10.8	11.7	-	-	21.5	55.7
	3.50	71.9	0	16.7	5.5	-	-	28.1	79.2
	3.875	75.9	0	19.4	0.0	-	-	34.6	100.0

TABLE A-II (Continued)

Experiment No. and Conditions	Time (hr)	Melt Composition (wt %)					Off Gas (g)		Percent Reduction
		M_2CO_3	M_2SO_3	M_2S	M_2SO_4	Fe	CO_2	H_2O	
19. 1.4 ℓ/min H_2(0.6) and H_2O(0.4), 650°C, 1 atm, no sulfide, 2.4% Fe ($FeSO_4$), Make-up-5	0.00	72.7	0	0.5	26.4	-	-	-	0.0
	3.00	70.2	0	1.6	23.5	-	-	-	11.0
	6.00	67.1	0	6.2	17.4	-	-	-	34.1
	9.00	71.9	0	18.9	0.7	-	-	-	97.3
20. 1.4 ℓ/min H_2, 600°C, no sulfide, 1 atm, 0.14 moles $Ti(SO_4)_2$, Make-up-8	0.00	67.5	0	0.0	32.0	-	-	0.0	0
	7.00	66.5	0	0.5	32.8	-	-	3.5	0
21. 1.4 ℓ/min H_2, 650°C, no sulfide, 1 atm, 4.8% Fe($FeSO_4$), Make-up-6	0.00	70.5	0	0.1	23.4	-	-	0.0	0.0
	1.25	73.8	0	2.5	21.0	4.52	-	3.7	10.3
	2.25	67.1	0	5.7	16.1	4.77	-	10.2	31.2
	3.00	74.2	0	8.5	11.4	4.90	-	15.8	51.3
	3.75	72.0	0	13.8	5.2	4.70	-	22.5	77.8
	4.25	70.5	0	17.5	0.0	-	-	27.6	100.0
	4.75	69.4	0	18.3	0.0	-	-	29.3	100.0
22. 1.4 ℓ/min H_2, 600°C, no sulfide, 1 atm, 0.14 mole $CoSO_4$, Make-up-8	0.00	71.8	0	0.1	26.5	-	-	0.0	0.0
	5.00	72.5	0	0.3	26.4	-	-	2.4	3.8
	13.75	75.0	0	3.7	20.3	-	-	10.7	23.4
	20.00	75.0	0	8.8	14.8	-	-	20.5	44.2
	23.50	74.9	0	12.8	9.9	-	-	26.1	62.6
	26.50	76.3	0	16.7	7.1	-	-	30.1	73.2
23. 1.4 ℓ/min H_2, 600°C, 1 atm, 0.14 mole GeO_2, Make-up-9	0.00	67.5	0	0.0	26.0	-	-	0.0	0.0
	3.00	61.8	0	0.1	25.8	-	-	1.5	0.7
	9.25	66.1	0	1.6	20.5	-	-	4.8	20.8
	21.00	67.2	0	4.5	19.8	-	-	12.8	23.8
	29.50	69.4	0	7.9	14.5	-	-	20.1	44.2
24. 1.4 ℓ/min H_2, 650°C, no sulfide, 1 atm, 1.3% Fe($FeSO_4$), Make-up-4	0.00	69.6	0	0.0	24.7	0.98	-	0.0	0.0
	1.75	78.8	0	1.3	22.6	-	-	3.0	8.5
	2.75	-	-	-	-	-	-	6.3	-
	3.75	75.7	0	6.0	16.4	1.29	-	11.9	33.6
	4.50	75.9	0	9.5	12.0	1.25	-	17.9	51.4
	5.25	76.5	0	14.6	6.8	1.40	-	24.8	72.5
	6.00	77.4	0	18.5	1.4	-	-	31.7	94.5
	6.50	78.1	0	21.1	0.0	-	-	34.6	100.0

TABLE A-II (Continued)

Experiment No. and Conditions	Time (hr)	Melt Composition (wt %)					Off Gas (g)		Percent Reduction
		M_2CO_3	M_2SO_3	M_2S	M_2SO_4	Fe	CO_2	H_2O	
25. 2.9 ℓ/min H_2, 600°C, no sulfide, 2.4% Fe as $FeSO_4$, 1 atm, Make-up-12 Packed bomb	0.00	-	-	-	-	-	-	0.00	0.0(2)
	0.167	-	-	-	-	-	-	0.25	1.7(2)
	0.333	-	-	-	-	-	-	0.95	6.5(2)
	0.50	-	-	-	-	-	-	1.73	11.8(2)
	0.75	-	-	-	-	-	-	3.05	20.9(2)
	1.00	-	-	-	-	-	-	4.81	32.9(2)
	1.25	-	-	-	-	-	-	6.67	45.7(2)
	1.50	-	-	-	-	-	-	8.78	60.1(2)
	1.75	-	-	-	-	-	-	10.80	74.0(2)
	2.00	-	-	-	-	-	-	12.86	88.1(2)
	2.167	-	-	-	-	-	-	13.68	93.7(2)
	2.333	-	-	-	-	-	-	14.36	98.4
26. 1.4 ℓ/min H_2, 650°C, 22.5% sulfide, 1 atm, 2.4% Fe ($FeSO_4$) Make-up-13	0.00	51.3	0	22.9	25.7	-	-	0.0	0.0
	0.25	48.7	0	25.1	24.0	-	-	3.9	6.6
	0.75	50.7	0	28.7	19.8	2.74	-	10.2	23.0
	1.25	52.5	0	32.4	15.8	-	-	16.9	38.5
	1.75	49.0	0	34.0	10.8	-	-	23.5	58.0
	2.25	50.3	0	38.6	5.8	-	-	30.2	77.4
	2.75	50.8	0	42.2	1.1	-	-	35.6	95.7
27. 1.4 ℓ/min H_2, 600°C, no sulfide, 1 atm, 0.14 mole Rb_2CO_3, Make-up-9	0.00	75.0	0	0	24.2	-	-	0.0	0.0
	1.50	-	-	-	-	-	-	0.9	-
	4.00	-	-	-	-	-	-	2.3	-
	6.00	75.2	0	1.2	22.3	-	-	3.5	7.9
	9.00	73.3	0	3.1	20.8	-	-	5.8	14.0
	14.25	74.4	0	4.5	18.3	-	-	10.9	24.3
	21.25	67.3	0	8.0	13.1	-	-	18.8	45.5
	27.25	79.2	0	12.0	9.4	-	-	25.4	61.2
28. 1.4 ℓ/min H_2 and He, 600°C, 10% sulfide, 1/2 atm H_2, 2.4% Fe ($FeSO_4$), Make-up-11	0.00	65.0	0	9.9	25.3	-	-	0.0	0
	1.00	-	-	-	-	-	-	1.7	-
	2.00	63.0	-	11.3	24.0	-	-	3.5	5.1
	3.00	-	-	-	-	-	-	5.7	-
	4.00	63.3	0	13.7	20.9	-	-	8.2	17.4
	5.00	-	-	-	-	-	-	10.8	-
	6.50	66.7	0	16.8	16.6	-	-	15.0	34.2
	8.00	64.6	0	20.3	12.8	-	-	19.7	48.6
	9.50	65.4	0	23.1	8.9	-	-	24.2	64.8
29. 1.4 ℓ/min H_2 and He, 600°C, 10% sulfide, 1/4 atm H_2, 2.4% Fe ($FeSO_4$), Make-up-11	0.00	59.8	0	9.3	23.1	-	-	0.0	0.0
	2.50	-	-	-	-	-	-	3.0	-
	3.50	64.7	0	10.5	21.3	-	-	5.3	7.8
	5.00	-	-	-	-	-	-	8.0	-
	7.50	68.3	0	14.4	18.1	-	-	10.6	21.6
	11.50	69.7	0	18.4	13.9	-	-	18.0	39.8

TABLE A-II (Continued)

Experiment No. and Conditions	Time (hr)	Melt Composition (wt %)					Off Gas (g)		Percent Reduction
		M_2CO_3	M_2SO_3	M_2S	M_2SO_4	Fe	CO_2	H_2O	
30. 2.8 ℓ/min H_2, 600°C, 10% sulfide, 2 atm, 2.4% Fe ($FeSO_4$), Make-up-11	0.00	61.5	0	11.2	23.8	-	-	0.0	0.0
	0.75	61.1	0	13.8	21.3	-	-	4.7	10.5
	1.50	63.9	0	14.3	18.9	-	-	9.0	20.6
	2.50	60.3	0	21.7	13.4	-	-	16.0	43.7
	3.50	71.2	0	24.5	6.3	-	-	24.2	73.5
	4.00	67.2	0	25.2	3.2	-	-	28.5	86.6
31. 1.4 ℓ/min H_2, 600°C, 10% sulfide, 1 atm, 2.4% Fe ($FeSO_4$), Make-up-11	0.00	64.8	0	9.3	23.5	-	-	0.0	0.0
	0.75	71.6	0	10.1	22.9	-	-	2.6	6.8
	1.75	69.6	0	12.4	20.6	-	-	5.8	12.3
	2.75	67.4	0	15.4	18.0	-	-	9.7	23.5
	4.25	71.1	0	18.9	12.2	-	-	16.8	48.1
	5.75	67.5	0	24.0	6.6	-	-	24.0	71.9
32. 7.0 ℓ/min H_2, 600°C, 10% sulfide, 5 atm, 2.4% Fe ($FeSO_4$), Make-up-11	0.00	62.9	0	9.1	24.1	-	-	0.0	0.0
	0.50	68.5	0	10.3	22.0	-	-	4.1	7.8
	1.25	64.6	0	14.9	17.6	-	-	11.3	27.0
	2.00	64.5	0	21.6	10.1	-	-	20.3	58.1
	2.625	68.2	0	29.3	3.9	-	-	25.7	83.8
33. 14.0 ℓ/min H_2, 600°C, 10% sulfide, 10 atm, 2.4% Fe ($FeSO_4$), Make-up-11	0.00	64.6	0	9.2	24.5	-	-	0.0	0.0
	0.75	68.0	0	15.4	18.0	-	-	9.2	26.5
	1.50	69.6	0	25.3	5.4	-	-	25.6	78.0
	1.75	70.5	0	30.6	1.0	-	-	30.4	95.9
34. 1.4 ℓ/min He, 500°C, no sulfide, 1 atm, no iron, Make-up-14 (disproportion-ation)	0.00	80.2	25.3	0.0	0.55	-	-	-	2.3(3)
	1.00	78.4	25.3	0.0	0.58	-	-	-	2.3(3)
	3.00	77.9	22.5	0.1	1.49	-	-	-	13.1(3)
	5.50	76.5	20.1	0.8	4.76	-	-	-	22.4(3)
	8.50	77.4	14.7	1.5	8.2	-	-	-	43.2(3)
	12.50	75.7	9.9	2.2	11.7	-	-	-	61.8(3)
	16.25	77.1	7.4	2.9	14.6	-	-	-	71.4(3)
	21.25	77.9	4.6	3.8	16.8	-	-	-	82.2(3)
	24.00	77.4	3.2	3.6	17.4	0.0070	-	-	87.6(3)
	25.75	78.1	2.5	4.1	17.3	-	-	-	90.3(3)
	28.50	78.1	1.7	3.8	18.1	-	-	-	93.4(3)

TABLE A-II (Continued)

Experiment No. and Conditions	Time (hr)	Melt Composition (wt %)					Off Gas (g)		Percent Reduction
		M_2CO_3	M_2SO_3	M_2S	M_2SO_4	Fe	CO_2	H_2O	
35. 1.4 ℓ/min H_2, 500°C, no sulfide, 1 atm, no iron; Make-up-14 (disproportionation)	0.167	84.4	24.4	0.0	0.55	-	0.0[5]	0.0	2.6[4]
	3.00	82.1	19.4	1.2	5.2	-	3.1[5]	1.0	24.5[4]
	6.00	76.0	14.4	3.1	7.5	0.0033	9.6[5]	3.1	35.4[4]
	8.625	75.8	11.6	4.6	8.1	-	16.0[5]	5.2	38.2[4]
	14.50	78.3	3.4	8.7	8.7	-	34.0[5]	11.0	41.0[4]
	22.50	82.8	0.0	12.0	8.6	-	52.2[5]	16.9	40.6[4]
	30.00	86.7	0.0	11.7	8.6	-	53.4[5]	17.3	40.6[4]
36. 1.4 ℓ/min H_2, 500°C, no sulfide, 1 atm, 0.14 mole Fe_2O_3; Make-up-15 (disproportionation)	0.167	70.7	21.9	0.0	3.2	-	0.0	0.0	17.5[4]
	3.00	68.0	0.0	3.9	18.3	-	1.5	0.5	100.0[4]
	7.00	74.3	0.0	4.4	17.0	-	5.9	2.0	100.0[4]
37. 4.5 g/min tetralin, 450-600°C, no sulfide, iron at 600°C; Make-up-1	0.50[6]	87.1	0	0.0	-	-	-	-	-
	1.25[7]	87.6	0	0.0	-	-	-	-	-
	0.00[8]	79.4	0	0.0	-	-	-	-	-
	0.50[8]	80.2	0	0.0	-	-	-	-	-
	0.00[9]	70.0	0	0.1	-	-	-	-	-
	1.50[9]	72.0	0	0.2	-	-	-	-	-
38. 1.4 ℓ/min He, 552°C, no sulfide, 1 atm, no catalyst; Make-up-14	0.00	72.9	0	0.0	0.63	-	-	-	3.2[3]
	1.00	68.4	0	0.72	4.37	-	-	-	15.1[3]
	2.00	67.9	0	1.3	7.1	0.0018	-	-	35.6[3]
	3.50	64.8	0	2.0	11.6	-	-	-	61.2[3]
	5.00	78.2	0	2.7	14.1	-	-	-	65.3[3]
	7.50	79.6	0	3.2	16.3	-	-	-	79.4[3]
	10.25	80.0	0	3.8	17.2	-	-	-	85.4[3]
	23.50	82.2	0	4.3	19.7	-	-	-	100.0[3]
39. 1.4 ℓ/min He, 600°C, no sulfide, 1 atm, no iron; Make-up-14 (disproportionation)	0.083	76.8	22.6	0.0	1.18	-	-	-	5.8[3]
	0.25	79.3	18.4	0.8	5.43	-	-	-	23.3[3]
	0.50	79.3	10.0	2.3	11.7	-	-	-	58.3[3]
	0.75	80.1	7.5	2.5	13.7	-	-	-	68.8[3]
	1.00	79.0	5.9	2.7	14.8	0.0095	-	-	75.4[3]
	1.33	82.1	4.4	3.3	16.1	-	-	-	81.7[3]
	1.67	78.0	2.7	3.5	16.9	-	-	-	88.8[3]
	2.167	82.2	1.6	4.1	18.2	-	-	-	93.3[3]

TABLE A-II (Continued)

Experiment No. and Conditions	Time (hr)	Melt Composition (wt %)					Off Gas (g)		Percent Reduction
		M_2CO_3	M_2SO_3	M_2S	M_2SO_4	Fe	CO_2	H_2O	
40. 1.4 ℓ/min H_2, 650°C, no sulfide, 1 atm, 4.8% Fe_2O_3; Make-up-16 (reduction Fe_2O_3)	0.00	-	-	-	-	-	-	0.00	-
	0.25	-	-	-	-	-	-	0.14	-
	0.75	-	-	-	-	-	-	0.29	-
	2.00	-	-	-	-	-	-	0.66	-
	3.25	-	-	-	-	-	-	1.06	-
	4.50	-	-	-	-	-	-	1.43	-
	5.75	-	-	-	-	-	-	1.73	-
	6.75	-	-	-	-	-	-	1.92	-
	9.25	-	-	-	-	-	-	2.05 (11)	-
	11.75	-	-	-	-	-	-	2.22	-
	14.25	-	-	-	-	-	-	2.58	-
	∞ (10)	-	-	-	-	-	-	6.2	-
41. 1.4 ℓ/min He, 525°C, no sulfide, 2.4% Fe_2O_3, 1 atm; Make-up-15 (disproportionation)	0.083	73.0	21.4	0.2	4.54	-	-	-	20.1 (3)
	0.167	73.2	18.4	0.4	6.84	-	-	-	31.3 (3)
	0.333	75.5	15.4	1.0	9.34	-	-	-	42.5 (3)
	0.500	71.9	11.6	1.2	10.3	-	-	-	55.7 (3)
	0.667	69.1	10.4	1.5	12.2	-	-	-	61.2 (3)
	0.833	71.6	6.4	2.3	15.0	-	-	-	76.1 (3)
	1.167	71.5	0.2	3.3	18.4	-	-	-	99.3 (3)
42. 1.4 ℓ/min H_2, 750°C, no sulfide, no iron, 1 atm; Make-up-1	0.00	79.3	0	0.0	19.5	-	-	0.0	0.0
	0.75	83.2	0	1.6	17.7	-	-	2.6	9.2
	1.50	80.6	0	3.2	15.6	-	-	6.2	20.0
	2.25	82.0	0	5.8	12.1	-	-	10.2	37.9
	3.00	83.4	0	8.7	9.3	-	-	14.9	52.3
	3.75	88.4	0	12.6	5.4	-	-	18.4	72.3
	4.50	89.6	0	16.4	1.5	0.0088	-	23.4	92.3
	5.25	87.5	0	17.5	0.0	-	-	26.1	100.0
	5.75	86.9	0	17.5	0.0	-	-	26.1	100.0
43. 1.4 ℓ/min H_2, 600°C, 1 atm, 2.4% Fe(Fe_2O_3), no sulfide; Make-up-9	0.00	72.5	0	0.0	24.9	-	-	0.0	0.0
	1.50	72.0	0	0.2	24.3	-	-	1.1	2.4
	3.00	72.2	0	0.4	23.3	-	-	2.7	6.3
	4.50	69.2	0	1.5	22.0	-	-	5.1	11.8
	6.00	71.7	0	3.6	19.7	-	-	9.3	21.0
	6.50	75.2	0	4.5	18.1	-	-	11.2	27.3
	7.50	72.3	0	6.8	14.8	-	-	15.9	40.5
	8.50	76.3	0	9.2	11.0	-	-	20.3	55.7
	9.50	77.1	0	12.4	6.4	-	-	25.6	73.3
	10.50	75.7	0	14.3	1.5	-	-	31.1	93.8

TABLE A-II (Continued)

Experiment No. and Conditions	Time (hr)	Melt Composition (wt %)					Off Gas (g)		Percent Reduction
		M_2CO_3	M_2SO_3	M_2S	M_2SO_4	Fe	CO_2	H_2O	
44. 1.4 ℓ/min CO, 600°C, 1 atm no catalyst, no sulfide; Make-up-1	0.00	73.2	0	0.0	26.1	-	0.0	-	0
	3.25	-	-	-	-	-	2.0	-	-
	19.00	73.1	0	1.0	23.5	-	14.6	-	10.0
	27.00	73.3	0	1.8	23.1	-	20.9	-	11.5
	43.00	76.8	0	3.8	20.3	-	(36.4)	-	22.2
	50.25	77.1	0	4.5	19.1	-	44.0	-	26.8
	58.25	83.2	0	5.8	17.0	-	56.4	-	34.9
	73.50	79.4	0	9.2	12.2	-	78.1	-	53.3
	81.50	78.0	0	11.5	9.74	-	88.0	-	62.8
	96.50	77.6	0	14.3	5.48	-	104.6	-	78.9
	104.50	82.6	0	16.2	3.37	-	112.1	-	87.0
45C 1.4 ℓ/min CO, 1 atm, no sulfide, no catalyst; Make-up-1	0.00	74.1	0	0.0	25.2	-	0.0	-	0.0
	2.00	-	0	-	-	-	4.7	-	-
	5.00	76.7	0	1.8	22.2	-	16.8	-	11.9
	6.75	78.4	0	3.7	19.4	-	29.6	-	23.0
	8.00	82.2	0	6.3	15.7	0.0065	43.9	-	37.7
	8.00 (12)	80.0	0	7.2	14.8	-	43.9	-	41.3
	9.50	87.7	0	10.9	8.2	-	66.0	-	67.5
	11.00	-	0	-	-	-	94.7	-	-
	11.50	86.3	0	18.8	0.0	-	97.5	-	100.0
46C 1.4 ℓ/min CO, 700°C, 1 atm, no sulfide, 2.4% Fe ($FeSO_4$); Make-up-5	0.00	80.9	0	0.0	24.7	1.25	0.0	-	0.0
	3.00	72.8	0	1.7	21.8	2.44	13.7	-	11.7
	4.50	79.3	0	2.9	19.6	-	23.1	-	20.6
	5.50	81.0	0	4.5	17.8	-	29.1	-	27.9
	7.00	76.4	0	6.6	15.6	2.51	37.8	-	36.8
	9.00	80.4	0	8.2	13.8	-	48.4	-	44.1
	9.50	83.1	0	7.2	11.8	-	51.2	-	52.2
	11.50	83.6	0	9.1	7.06	-	64.1	-	71.3
	13.50	85.6	0	16.2	2.66	-	77.9	-	89.1
	15.50	88.8	0	20.0	0.0	2.16	89.2	-	100.0
47C 1.4 ℓ/min CO, 700°C, 1 atm, 10% sulfide, no catalyst; Make-up-10	0.00	68.7	0	10.3	25.4	-	0.0	-	0.0
	1.00	75.7	0	12.0	20.1	-	17.0	-	20.9
	2.00	73.6	0	18.4	12.6	-	46.8	-	50.4
	2.625	75.8	0	21.5	6.4	-	67.6	-	74.8
	2.75	-	-	-	-	-	74.3	-	-
	3.00	72.3	0	24.2	3.4	-	83.1	-	86.6
	3.25	-	-	-	-	-	91.6	-	-
	3.50	72.5	0	30.3	0.6	-	98.9	-	97.6
	3.75	-	-	-	-	-	103.7	-	-
	4.00	72.5	0	33.3	0.0	-	106.2	-	100.0

TABLE A-II (Continued)

Experiment No. and Conditions	Time (hr)	Melt Composition (wt %)					Off Gas (g)		Percent Reduction
		M_2CO_3	M_2SO_3	M_2S	M_2SO_4	Fe	CO_2	H_2O	
48C 1.4 ℓ/min CO, 700°C, 1 atm, 10% sulfide, 2.4% Fe ($FeSO_4$); Make-up-11	0.00	69.8	0	7.7	25.4	-	0.0	-	0.0
	1.00	64.7	0	13.5	22.7	-	10.3	-	10.6
	2.00	64.6	0	13.6	20.2	-	19.7	-	20.5
	3.50	65.5	0	16.5	16.2	-	34.1	-	36.2
	5.00	67.8	0	21.3	12.0	-	49.2	-	52.8
	6.50	69.7	0	23.4	6.9	-	66.0	-	72.8
	8.00	63.7	0	28.2	1.0	-	84.5	-	96.1
49C 1.4 ℓ/min CO and H_2, 700°C 10% sulfide, no catalyst; Make-up-10	0.00	65.3	0	10.5	25.9	-	0.0	0.0	0.0
	1.00	66.5	0	14.4	19.7	-	6.8	6.8	23.9
	2.00	70.0	0	19.9	11.7	-	14.2	16.5	54.8
	2.50	-	-	-	-	-	-	20.6	-
	3.00	75.2	0	25.4	3.2	-	25.8	24.5	87.3
	3.50	73.0	0	29.1	0.6	-	31.2	27.4	97.7
	CO ∞ (10)						105.5	0.0	100.0
	H_2 ∞ (10)						0.0	43.2	100.0
51. 1.4 ℓ/min CO, 700°C, 1 atm, no sulfide, 0.14 mole $SnSO_4$; Make-up-8	0.00	68.8	0	0.3	23.2	-	0.0	-	0.0
	5.00	69.4	0	2.0	17.7	-	21.2	-	23.7
	6.75	70.9	0	2.9	14.7	-	29.3	-	36.6
	8.00	77.6	0	4.4	13.9	-	37.8	-	40.1
	9.50	78.8	0	4.3	11.5	-	45.6	-	49.8
	12.25	81.8	0	5.8	6.23	-	60.7	-	73.3
	13.75	84.7	0	5.9	3.12	-	67.9	-	86.6
52. 1.4 ℓ/min CO, 700°C, 1 atm, no sulfide, 2.4% Fe ($FeSO_4$); Make-up-5	0.00	71.8	0	0.2	24.4	-	-	0.0	0.0
	1.00	66.6	0	2.4	21.3	-	-	5.3	12.7
	1.75	66.3	0	5.8	16.9	-	-	11.6	30.7
	2.25	71.2	0	9.5	12.7	-	-	17.8	48.0
Pyrolysis; melt samples at 700, 870, and 940°C, respectively	0.00	71.2	0	9.5	12.7	-	-	-	0.0
	1.183	73.4	0	10.6	9.15	-	-	-	27.5
	1.733	85.6	0	17.1	1.81	-	-	-	85.8
53. 1.4 ℓ/min $H_2 + H_2O$, 650°C, 1 atm, 10% sulfide, 2.4% Fe ($FeSO_4$); Make-up-11	0.00	69.3	0	8.5	24.5	-	-	-	0.0
	3.50	64.7	0	8.6	22.3	-	-	-	9.0
	5.75	64.6	0	12.0	19.3	-	-	-	21.2

TABLE A-II (Continued)

Experiment No. and Conditions	Time (hr)	Melt Composition (wt %)					Off Gas (g)		Percent Reduction
		M_2CO_3	M_2SO_3	M_2S	M_2SO_4	Fe	CO_2	H_2O	
54. 1.4 ℓ/min CO then H_2, 1 atm, no sulfide, 840°C, no iron; Make-up-1	0.00	72.9	0	0.0	25.3	-	0.0	-	0.0
	1.00	74.8	0	1.9	22.3	-	-	-	11.9
	1.33	-	-	-	-	-	17.4	-	-
	2.50	75.5	0	5.2	18.1	-	27.1	-	28.4
	3.50	77.5	0	8.2	14.2	-	40.7	-	43.9
	0.00	77.5	0	8.2	14.2	-	-	0.0	43.9
	0.33	83.7	0	13.8	5.8	0.013	-	7.3	77.1
	0.50	-	-	-	5.8	-	-	11.8	-
	0.67	78.5	0	21.7	0.0	-	-	14.4	100.0
55. 1.4 ℓ/min CO and He, 700°C 1/2 atm CO, 10% sulfide, no iron; Make-up-10	0.00	71.0	0	11.0	26.3	-	0.0	-	0.0
	1.00	-	-	-	-	-	6.4	-	-
	2.00	73.6	0	10.5	20.6	-	15.4	-	21.7
	3.00	77.0	0	15.4	18.5	-	25.9	-	29.7
	3.50	-	-	-	-	-	32.0	-	-
	4.50	75.6	0	17.7	13.2	-	45.6	-	49.8
	6.00	75.0	0	21.6	5.8	-	68.7	-	77.9
	7.00	71.7	0	24.6	2.2	-	86.5	-	91.6
56. 0.35 ℓ/min He, 700°C, 1 atm, coke, no catalyst; Make-up-1	0.00	68.8	0	0.0	25.6	-	0.0	-	0.0
	1.00	77.7	0	2.8	20.6	-	6.5	-	19.5
	2.00	80.0	0	8.3	10.3	-	13.7	-	59.8
	2.50	79.1	0	11.9	6.7	-	19.2	-	73.8
	3.00	81.0	0	15.8	4.0	-	22.5	-	84.4
	3.50	80.0	0	15.7	2.0	-	26.1	-	92.2
	6.50	78.0	0	17.7	0.0	-	37.0	-	100.0
57. 0.35 ℓ/min He, 700°C, 1 atm, coke, 2.4% Fe($FeSO_4$); Make-up-5	0.00	73.0	0	0.1	25.8	-	0.0	-	0.0
	0.75	76.9	0	3.7	13.6	-	10.7	-	47.3
	1.75	76.7	0	12.1	2.9	-	24.2	-	89.1
	2.50	78.9	0	16.9	0.0	-	29.7	-	100.0
	3.00	76.8	0	17.1	0.0	-	31.2	-	100.0
58. 1.4 ℓ/min CO_2 and H_2, 0.9 atm H_2, 700°C, 2.4% Fe ($FeSO_4$), no sulfide; Make-up-5	0.00	73.2	0	0.0	26.0	-	-	0.0	0.0
	1.00	74.2	0	1.0	23.3	-	-	5.2	10.4
	1.75	74.4	0	2.0	20.5	-	-	10.5	21.2
	2.75	76.1	0	3.3	16.9	-	-	18.1	35.0
	3.75	72.4	0	5.8	12.9	-	-	26.3	50.4
	4.50	82.0	0	9.7	4.90	-	-	33.5	81.2
	4.75	81.3	0	15.7	0.0	-	-	36.0	100.0
	5.75	84.8	0	15.3	0.0	-	-	41.3	100.0

TABLE A-II (Continued)

Experiment No. and Conditions	Time (hr)	Melt Composition (wt %)					Off Gas (g)		Percent Reduction
		M_2CO_3	M_2SO_3	M_2S	M_2SO_4	Fe	CO_2	H_2O	
59. 0.35 ℓ/min	0.00	-	-	-	24.5	-	0.0	-	0
He, 600°C,	1.00	-	-	-	-	-	2.3	-	-
1 atm, coke,	2.00	-	-	-	25.1	-	3.6	-	0
2.4% $Fe(FeSO_4)$;	3.00	-	-	-	-	-	4.4	-	-
Make-up-5	4.00	-	-	-	-	-	5.0	-	-
	5.50	-	-	-	23.2	-	6.0	-	7.6
	21.50	-	-	-	19.4	-	14.6	-	22.7
	28.50	81.4	-	4.3	17.3	-	16.5	-	31.1
60. 1.4 ℓ/min	0.00	71.7	0	0.0	26.7	-	-	0.0	0.0
H_2, 650°C, no	1.50	-	-	-	25.1	-	-	1.7	6.0
sulfide, 0.23%	3.50	74.9	0	2.8	22.1	0.24	-	6.3	17.2
$Fe(FeSO_4)$,	5.75	-	-	-	15.4	-	-	15.7	42.3
1 atm;	6.50	77.0	0	11.4	12.6	0.25	-	18.4	52.8
Make-up-3	7.50	-	-	-	8.4	0.26	-	23.3	68.5
	8.50	80.5	0	16.9	4.4	0.26	-	28.3	83.5
61. 1.4 ℓ/min	0.00	64.1	0	0.0	25.6	-	-	0.0	0.0
H_2, 650°C, no	3.25	-	-	-	23.4	-	-	3.6	8.6
sulfide or iron,	6.75	62.3	0	4.2	19.6	0.0028	-	9.6	23.4
1 atm;	9.25	-	-	-	16.1	0.0036	-	15.8	37.1
Make-up-1	11.75	62.3	0	11.7	9.8	0.0092	-	24.0	61.7
	13.25	-	-	-	6.0	0.0203	-	29.0	76.6
	14.00	63.9	0	17.5	3.8	-	-	31.8	85.2
62. 0.35 ℓ/min	0.00	61.8	0	0.7	25.0	-	0.0	-	0.0
He, 1 atm,	0.25	-	-	-	11.0	-	17.6	-	56.0
800°C, no	0.50	65.6	0	13.3	0.7	-	30.8	-	97.2
catalysts;									
Make-up-1 (coke)									
63. 1.4 ℓ/min	0.00	76.2	0	0.0	26.0	-	-	0.0	0.0
H_2, 650°C,	2.00	-	-	-	24.1	-	-	2.4	7.3
1 atm, no	4.50	68.6	0	1.5	20.9	0.068	-	7.2	19.6
sulfide,	6.00	-	-	-	18.8	-	-	11.0	27.7
0.05% $Fe(FeSO_4)$;	7.25	79.0	0	5.6	16.3	0.105	-	14.5	37.3
Make-up-2	9.00	-	-	-	12.8	-	-	19.0	50.8
	10.50	74.3	0	9.9	9.4	0.109	-	23.5	63.1
	12.00	81.3	0	12.1	5.6	-	-	28.4	78.5
64. 1.4 ℓ/min	0.00	78.8	0	0.0	25.8	-	-	0.0	0.0
H_2S, 1 atm,	0.25	59.2	0	13.8	26.2	-	-	6.8	0.0
600°C, no	0.50	49.2	0	28.8	25.7	-	-	13.4	1.0
catalysts;	1.00	30.2	0	45.0	24.8	-	-	22.0	3.8
Make-up-1									

TABLE A-II (Continued)

Experiment No. and Conditions	Time (hr)	Melt Composition (wt %)					Off Gas (g)		Percent Reduction
		M_2CO_3	M_2SO_3	M_2S	M_2SO_4	Fe	CO_2	H_2O	
65. 1.4 ℓ/min H_2, 1 atm, 650°C, no sulfide, 2.4% Fe ($FeSO_4$), 0.6% CaO; Make-up-1	0.00	75.7	0	0.0	23.8	-	-	0.0	0.0
	0.75	-	-	-	-	-	-	1.1	-
	1.75	-	-	-	22.3	-	-	4.3	6.3
	2.75	74.6	0	2.6	19.4	-	-	8.6	18.5
	3.50	-	-	-	16.1	-	-	13.3	32.4
	4.25	76.5	0	7.7	11.9	-	-	18.9	53.4
	4.75	72.9	0	10.1	8.2	-	-	-	65.5
66. 1.4 ℓ/min H_2, 650°C, no sulfide, 1 atm, 6% Fe($FeSO_4$); Make-up-7	0.00	63.6	0	0.0	23.6	-	-	0.0	0.0
	1.25	65.2	0	0.4	23.1	-	-	2.5	2.1
	2.25	62.8	0	1.2	21.0	-	-	7.8	14.8
	3.00	59.2	0	3.0	18.6	-	-	13.1	21.2
	3.75	64.1	0	5.9	13.6	-	-	19.7	42.4
67. 1.4 ℓ/min NH_3, 650°C, no sulfide, 2.4% Fe ($FeSO_4$); Make-up-5	0.00	76.7	0	0.0	24.3	-	-	-	0.0
	1.00	70.5	0	0.0	25.3	-	-	-	0.0
68. Inert gas purge, coke, 800°C, no sulfide, 1 atm, 2.4% Fe($FeSO_4$); Make-up-5	0.00[13]	69.3	0	0.0	24.1	-	-	-	0.0
	5.00[13]	70.1	0	4.9	15.9	-	-	-	34.0
	8.00[13]	80.4	0	8.9	10.0	-	-	-	58.5
	12.00[13]	-	-	-	4.0	-	-	-	83.4
	16.00[13]	74.6	0	13.7	0.0	-	-	-	100.0
	20.00[13]	74.0	0	15.6	0.0	-	-	-	100.0
	25.00[13]	76.0	0	11.9	0.0	-	-	-	100.0
	30.00[13]	69.7	0	17.5	0.0	-	-	-	100.0

(1) Lost some product gas

(2) Based upon H_2O evolution

(3) Percent disproportionation; based upon sulfite results and the sulfate and sulfite results of the first sample

(4) Percent disproportionation, based upon sulfate results (theoretical = 21.2% based upon first sample analysis)

(5) Percent reduced, based upon water evolution (theoretical = 32.4 g, not accounting for samples)

(6) 450°C

(7) 500°C

(8) 600°C

(9) 600°C with 2.4% $Fe(FeSO_4)$

(10) Theoretical

(11) Not including 0.44 g evolved with overnight He purge

(12) After overnight He purge

(13) Time in minutes